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(54) Ethylene-alpha-olefin copolymer composition

Zusammensetzungen aus Äthylen-Copolymeren

Composition à base de copolymères d'éthylène

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(73) Proprietor: **SUMITOMO CHEMICAL COMPANY, LIMITED**
Chuo-ku Osaka 541 (JP)

(72) Inventors:
- **Fukushima, Nobuo**
  Ootsu-shi (JP)
- **Kitamura, Shuji**
  Ibaraki-shi (JP)
- **Nakae, Kiyohiko**
  Nishinomiya-shi (JP)
- **Ogawa, Tadatoshi**
  Takatsuki-shi (JP)
- **Kotani, Kozo**
  Toyonaka-shi (JP)
- **Hosono, Hidekazu**
  Toyonaka-shi (JP)

(74) Representative: **Henkel, Feiler, Hänzel & Partner**
Möhlstrasse 37
81675 München (DE)

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Description

The present invention relates to an ethylene-α-olefin copolymer composition. More particularly, the present invention relates to ethylene-α-olefin copolymer compositions excellent in processability, impact strength, tensile strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, tear strength, transparency, heat-sealing characteristics and chemical characteristics such as chemicals resistance.

Being excellent in melt rheology characteristics as well as in physical and chemical properties, low density polyethylenes manufactured by the high pressure method (hereinafter referred to as "high pressure polyethylene") have been used for various uses such as films, sheets, pipes, blow bottles, injection molded products, coating materials for steel pipes and foam-molded materials. As mentioned above, high pressure polyethylenes are excellent in melt rheology characteristics, and therefore, they are excellent in processability. When used for extrusion processing or injection molding, their production efficiency is high, resulting in relatively low electricity consumption. In blown film processing, the above polyethylenes give good bubble stability. In cast film processing and extrusion lamination processing, there is only slight "neck-in". In blow molding, these polyethylenes give good parison stability. However, when they are processed into molded products, their mechanical strengths, such as tensile strength and impact strength, are relatively low and accordingly these products can not be used in thin forms.

High pressure polyethylenes have various other problems. They are used in many fields as films. Films of high pressure polyethylenes are required to have the following properties in recent, highly developed automatic packaging systems.

(1) Good heat-sealing property at low temperatures.
(2) High sealing strength in a condition where heat-sealed portions are not cooled sufficiently and therefore are not solidified yet (this strength is called "hot tack" strength). Hot tack strength is required because filling of contents and heat sealing are done almost at the same time.
(3) Sealing strength in a state where heat-sealing portions are contaminated with oils and the like, in packaging of oils and the like. (This strength is called heat sealing strength in contaminated condition). However, high pressure polyethylenes are not satisfactory in hot tack and heat sealing strength in contaminated condition. When these polyethylenes are used in blow bottles, pipes and injection molded products, they are inadequate in environmental stress cracking resistance, therefore, cause occasional troubles and are susceptible to attack by chlorine water. Further, they are not sufficient in creep characteristics, which makes them unusable in pipes of high internal pressure. When high pressure polyethylenes are used as coating materials for steel pipes, their low temperature resistance is not satisfactory, which makes their use in very cold climatic areas improper. In their use as coating materials for electric wires, troubles occur at times due to improper environmental stress cracking resistance and water-tree resistance.

To improve these defects, some attempts have been made. However, the quality is still not at a satisfactory level. For improvement of these defects, the following polymerization methods have been adopted.

(1) Polymerization of ethylene and other polymerizable monomer such as vinyl acetate.
(2) Method in which ethylene and acrylic acid (or methacrylic acid) are polymerized followed by conversion to a salt with a metal, namely an ionomer.

The former method still has many problems such as (a) reduction of tear strength, rigidity and heat resistance of films, (b) occurrence of corrosion of extruder and smell in processing due to liberation of acetic acid and (c) occurrence of blocking due to sticky film surface and cold flow. The latter method has problems of reduction of thermal stability and weather resistance and of high cost.

Also for improvement of the defects of high pressure polyethylenes, there were made proposals in which a high pressure polyethylene is mixed with another α-olefin polymer such as high density polyethylene, polypropylene, polybutene, or a rubber. However, an improvement in one defect causes another problem and no satisfactory answer has been attained.

As resins which have low densities about equal to those of high pressure polyethylenes, there are known resins which are prepared by co-polymerizing ethylene and an α-olefin under a medium to low pressure using a transition metal catalyst. (Hereinafter, such are abbreviated as "ethylene-α-olefin copolymers"). The copolymers produced with a vanadium catalyst are low in degree of crystallization, and have problems in heat resistance, weather resistance and mechanical strengths. The ethylene-α-olefin copolymers produced under normal polymerization conditions with a titanium catalyst, having generally narrow molecular weight distributions (narrower than those of high pressure polyethylenes), are relatively excellent in mechanical strengths but poor in melt rheology characteristics and have many problems in processing. In blown film processing, a large quantity of electricity is needed, output is reduced or bubble stability is lost. In high speed processing, "shark skin" appears on film surfaces, thereby decreasing product values. Also in blow molding, parison stability is lost, or surfaces of molded products turn to "shark skin" and product values are lost. In injection molding, processing temperatures need to be largely raised because of poorer flow property under high pressures as compared with high pressure polyethylenes, which requires more heat energy and moreover causes resin deterioration.

Trials have been made in recent years for solving these problems by improving extruders, screws and dies. These approaches require a large amount of expenditures and moreover techniques have not been fully developed. Further, various other problems such as the following have been encountered:

(1) with respect to mechanical strengths of films produced, balancing of machine direction (MD) and transverse direction (TD) is difficult and the tear strength of MD is poorer than that of high pressure polyethylenes, and
(2) film transparency is inferior to that of high pressure polyethylenes, because the ethylene-α-olefin copolymer of narrow molecular weight distribution has a faster crystalization speed than high pressure polyethylenes and causes melt fracture more easily.

Low density ethylene-α-olefin copolymers are difficult to obtain under normal polymerization conditions using a chromium catalyst, because copolymerizability between ethylene and α-olefin is generally lower with chromium catalysts than with titanium catalyst. When a chromium-titanium catalyst is used in order to overcome this problem, ethylene-α-ethylene copolymers obtained have wider molecular weight distributions than copolymers produced with a titanium catalyst and have slightly improved processability. However, their mechanical strengths largely worsen and their physical properties are not much different from those of high pressure polyethylenes and these copolymers provide film sheets and bottles inferior in transparency.

For attempting to improve the transparency of these copolymers, when the quantity of an α-olefin is largely increased in polymerization and the density of the copolymer obtained is reduced, only a sticky copolymer having much deteriorated mechanical strengths is produced.

According to the knowledge of the present inventors, ethylene-α-olefin copolymers polymerized under a medium to low pressure using a transition metal catalyst, have non-uniform component distributions. Namely in these copolymers, the number of short chain branching per 1000 carbon atoms (excluding methyl groups at the ends) (hereinafter referred to as "S.C.B." for brevity) varies depending upon molecular weight, and generally lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. This phenomenon is considered to be due to that α-olefins tend to act as a chain transfer agent or act even to active sites of catalyst to which molecular weight regulators such as hydrogen tend to act. (cf. Reference Example 1).

Because of the above phenomenon, ethylene-α-olefin copolymers polymerized with the α-olefin concentration increased with an aim to reduce to a large extent the density of copolymers produced, only give such products as those having increased S.C.B. in their lower molecular weight components, thereby having increased solubility in solvents and poor mechanical strengths and causing surface stickiness. This tendency is particularly remarkable in those ethylene-α-olefin copolymers which are polymerized with a catalyst giving wider molecular weight distributions. One of the reasons for poor mechanical strengths of ethylene-α-olefin copolymers having wide molecular weight distributions will be explained by the above fact.

As described above, ethylene-α-olefin copolymers having densities about equal to those of high pressure polyethylenes and synthesized under a medium to low pressure with a transision metal catalyst, can not satisfy all of processability, mechanical strengths and transparency. For instance, lowering of molecular weight for improvement of processability results in large reduction in mechanical strengths and disappearance of said copolymer characteristics. Broadening of molecular weight distribution leads to large reduction in mechanical strengths as well (cf. Reference Example 2), and moreover transparency worsens and surfaces of molded products get sticky. Thus, both of processability and physical properties are not met together yet, and any low density ethylene-α-olefin copolymer excellent in processability and mechanical strengths have not yet been provided.

As described above, high pressure polyethylenes are excellent in rheology characteristics and processability but relatively poor in mechanical strengths. On the other hand, ethylene-α-olefin copolymers polymerized under a medium to low pressure with a transition metal catalyst and having density about equal to those of high pressure polyethylenes, have excellent mechanical strengths due to their narrower molecular weight distributions but are poor in processability. These property differences are considered to originate from molecular structures of polymers.

High pressure polyethylenes are obtained from radical polymerization under a pressure of about 1500 to 4000 bar at a temperature of about 150° to 350°C in an autoclave or a tubular reactor. Their molecular structures are very complicated and, in spite of being homopolymers of ethylene, have short chain branches which are alkyl groups of 1 to 6 carbon atoms. These short chain branches affect crystallinities and therefore densities of polymers. The distribution of short chain branching of high pressure polyethylenes is relatively even, and both lower molecular weight components and high molecular weight components have almost similar numbers of branches.

Another important feature of high pressure polyethylenes is that the polyethylenes also have long chain branches in complicated structures. Identification of these long chain branches is difficult, but these branches are considered to be alkyl groups of which lengths vary from about lengths of main chains to lengths having carbon atoms of over several thousands. The presence of these long chain branches largely affects melt rheology characteristics of polymers and this is one of the reasons for the excellent processability of high pressure method polyethylenes.

On the other hand, ethylene-α-olefin copolymers synthesized under a medium to low pressure with a transition metal catalyst and having densities about equal to those of high pressure polyethylenes, are obtained by copolymerizing ethylene and an α-olefin under a medium to low pressure of about 5 to 150 bar and at 0°-250°C normally at a relatively low temperature of 30° to 200°C with a transition metal catalyst in an autoclave or a tubular reactor. Their molecular structures are relatively simple. These ethylene-α-olefin copolymers seldom possess long chain branches and have only short chain branches. These short chain branches are not formed through complicated reaction processes as so in high pressure polyethylenes, but are controlled by the kind of an α-olefin to be used in the copolymerization. As an example, in a copolymerization between ethylene and butene-1, short chain branches formed are normally ethyl branches. These branches could be hexyl branches as a result of dimerization of butene-1). Short chain branches formed control crystallinities and densities of polymers.

Distribution of short chain branches is also affected by the nature of a transition metal catalyst used in the copolymerization, the type of polymerization and the temperature of polymerization. Different from the case of high pressure polyethylenes, the distribution is wide. Namely, as a general trend, lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. (cf. Reference Example 1).

Ethylene-α-olefin copolymers obtained by copolymerizing ethylene and an α-olefin under a medium to low pressure with a transition metal catalyst and having densities about equal to those of high pressure polyethylenes, have come to be practically used. Therefore, the conventional classification that polyethylene resins having densities of 0.910 to 0.935 g/cm^3 fall in a category of high pressure polyethylenes, is improper and a new classification should be developed, mainly based on whether or not a polymer or resin has long chain branches. As low density polyethylenes substantially not having long chain branches, there are resins which are obtained by polymerization using a transition metal catalyst under a same high pressure and temperature as employed in the manufacture of high pressure method polyethylenes. These resins are also included in "ethylene-α-olefin copolymers" as defined by the present invention.

Presence or absence of long chain branches is clarified to a considerable extent by a theory of solution. As an example, the presence of long chain branches in an ethylene polymer can be known by using $[\eta]/[\eta]$, namely g_η^*. Herein, $[\eta]$ is the intrinsic viscosity of the ethylene polymer, and $[\eta]_l$ is the intrinsic viscosity of a reference linear polyethylene (high density polyethylene produced from homopolymerization of ethylene under a medium to low pressure with a Ziegler catalyst) having the same weight average molecular weight by the light scattering method. Molecules having more long chain branches have less spread in a solution, and therefore, their g_η^* is small. Normally, g_η^* of high pressure polyethylenes is 0.6 or less.

This method is useful, but practically the presence of long chain branches can be known more easily and clearly by a correlation between melt index and intrinsic viscosity of polymer. This correlation was shown in Reference Example 3. In there, the intrinsic viscosity of a high pressure polyethylene is far lower than that of the ethylene-α-olefin copolymer according to a medium to low pressure method having the same melt index, because the former polyethylene has long chain branches.

Due to the difference of presence or absence of long chain branches, high pressure polyethylenes and ethylene-α-olefin copolymers give largely different properties in melt rheology characteristics, crystallinity, solid mechanical properties and optical properties.

The present inventors made strenuous efforts with an aim to obtain polyethylenes which will solve the above-mentioned defects of polyethylenes, will have a processability equal to or better than that of high pressure polyethylenes, and will be excellent in tear strength, impact strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, chemicals resistance, transparency and heat-sealing characteristics. As a result, the present inventors have found that, by mixing (a) an ethylene-α-olefin copolymer having a relatively higher molecular weight and of which density, intrinsic viscosity, S.C.B., kind of α-olefin and (weight average molecular weight) /(number average molecular weight) are specified and (b) another ethylene-α-olefin copolymer having a relatively lower molecular weight and of which density, intrinsic viscosity, S.C.B., kind of α-olefin and (weight average molecular weight) /(number average molecular weight) are specified, in such a way that the ratio of S.C.B. of the former copolymer over S.C.B. of the latter copolymer is in a specified range, ethylene copolymer compositions can be obtained which have extremely good processability compared with the conventional polyethylenes, as well as very excellent physical and chemical properties such as tear strength, impact strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, chemicals resistance, transparency, and heat-sealing characteristics. The present inventors have also found that ethylene-α-olefin copolymer compositions substantially not having long chain branches and having a specific distribution of S.C.B. provide extremely good properties such as tensile strength, impact strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, chemicals resistance, transparency and heat-sealing characteristics, compared with the conventional polyethylenes, and therefore, with such ethylene-α-olefin copolymer compositions, improvement of processability by broadening of molecular weight distribution can be attained without deterioration of properties described above. Thus, the present invention has been achieved.

According to the present invention, there is provided an ethylene-α-olefin copolymer composition excellent in strength and having a density of 0.915 to 0.929 g/cm^3, a melt index of 0,1 to 30 g/10 min, and a melt flow ratio of 35 to 250, which comprises 10 to 70% by weight of at least one ethylene-α-olefin copolymer A and 90 to 30% by weight of at least one ethylene-α-olefine copolymer B; said copolymer A having a higher molecular weight than copolymer B and being a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms and having a density of 0.895 to 0.935 g/cm^3, an intrinsic viscosity $[n]_A$ of 1.2 to 6.0 dl/g, and the number of short chain branching per 1000 carbon atoms (S.C.B.) of 7 to 40 and a (weight average molecular weight)/(number average molecular weight) value of 2 to 10; said copolymer B being a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms and having a density of 0.910 to 0.955 g/cm^3, an intrinsic viscosity $[\eta]_B$ of 0.3 to 1.5 dl/g, S.C.B. of 5 to 35 and a (weight average molecuar weight)/(number average molecular weight) value of 2 to 10; said copolymer A and said copolymer B being selected in order to satisfy a condition that (S.C.B. of said copolymer A)/(S.C.B. of said copolymer B) is 0.6 to 1.7 and $[\eta]_A/[\eta]_B$ is 1.75 to 6.35, which copolymer composition has a g_η^* of at least 0.9 and a ratio of (SCB of higher molecular weight components)/(SCB of lower molecular weight components) of 0.6 to 0.8, wherein these SCB values are obtained by:
obtaining a curve of the molecular weight distribution by gel permeation chromatography, wherein the abscissa is the logarithm of the chain length (unit nm) calibrated with a standard polystyrene sample, and the ordinate is the relative weight fraction;
then obtaining fractions of lower and higher molecular weight by either one of the following methods:

1. in cases where curves of molecular weight distributions have one peak a lower molecular weight components side and a higher molecular weight components side are divided by a line drawn between the peak of the curve and the midpoint of a line drawn between the end of lower molecular weight components in the curve and the end of higher molecular weight components; and the ratio of areas of these two sides is the weight ratio of lower and higher molecular weight components; separately, fractions of the same sample are prepared by column fractionation; these fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions become closest to the weight ratio obtained above;
2. in cases where curves of molecular weight distributions have two peaks or more peaks including shoulders, a tangent line is drawn between the main two peaks of the higher molecular weight components side or between one peak and a shoulder of the same side, and then a perpendicular is drawn from a point where the distance between the GPC curve and the tangent line becomes largest; this perpendicular splits the lower molecular weight components side and the higher molecular weight components side, and the ratio of areas of these two sides becomes the weight ratio of these two components portions; when peaks are continuous and can not be detected (case of somewhat square curve), the technique of one peak distribution is applied; separately, fractions of the same sample are prepared by column fractionation; these fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions becomes closest to the weight ratio thus obtained; and then measuring the SCB of each group.

The present invention also provides a composition of copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms, having the following properties:

(1) density of 0.915 to 0.929 g/cm^3,
(2) intrinsic viscosity [η] of 0.7 to 4.0 dl/g,
(3) melt index of 0.1 to 30 g/10 min,
(4) the number of short chain branching per 1000 carbon atoms (S.C.B.) being 10 to 35,
(5) $[\eta]/[\eta]_l$ namely g_η^* being at least 0.9, where $[\eta]_l$ is an intrinsic viscosity of a linear polyethylene having the same weight average molecular weight measured by a light scattering method, and
(6) (S.C.B. of the higher molecular weight components)/(S.C.B. of the lower molecular weight components) being 0,6 to 0,8, wherein these two component groups are obtained by a molecular weight fractionation method.

The first feature of this invention is to provide an ethylene copolymer composition of which processability is about equal to or better than that of high pressure polyethylenes and of which physical and chemical properties such as tensile strength, impact strength, environmental stress cracking resistance, creep characteristics, tear strength, transparency, heat-sealing characteristics and chemicals resistance are very excellent.

The second feature of this invention is that, because the product of this invention is excellent in mechanical strengths, has a rigidity higher than those of high pressure polyethylenes and has a transparency about equal to that of high pressure polyethylenes, material saving can be expected with the product of this invention; for instance, when this product is used for films, the same performance can be obtained with the thickness of 10 to 20% thinner than that of high pressure polyethylenes.

The third feature of this invention is that, because the product of this invention has extrusion processability superior to that of relatively low density ethylene-α-olefin copolymers by the conventional technique, conventional extruders being used for high pressure polyethylenes can be utilized for the present product without any modification.

The fourth feature of this invention is that, because the present product, even if possessing a melt index lower than that of low density ethylene-α-olefin copolymers by the conventional technique, shows satisfactory flow properties in actual processing, it gives excellent bubble stability and mechanical strengths of machine and transverse directions can be easily balanced, whereby molded products can have a uniform quality.

The fifth feature of this invention is that, because a resin composition less sticky than low density ethylene-α-olefin copolymers by the conventional technique is obtained even when the density of the composition is lowered, the composition can be applied even for the usages where transparency, flexibility and impact characteristics are required.

In the attached drawings, Figs. 1 to 5 show curves of molecular weight distributions obtained from gel permeation chromatography. Broken lines in these figures are for dividing lower molecular weight components and high molecular weight components into two respective territories.

Fig. 6 is a typical example showing "distribution of S.C.B. against molecular weight" of an ethylene-α-olefin copolymer of the conventional technique.

Fig. 7 shows correlations between melt indices (MI) and tensile impact strengths of ethylene-α-olefin copolymers of the conventional technique, with their melt flow ratios (MFR) used as a parameter.

Fig. 8 shows correlations between MI and intrinsic viscosities [η] of a high pressure polyethylene and a linear polyethylene of the medium to low pressure method as a method for distinguishing these two polymers. In the figure, a broken line is drawn to separate two territories, the left side territory is for the high pressure polyethylene of the conventional technique and the right side territory is for the linear polyethylene of the medium to low pressure method.

The present invention will be explained in more detail below.

An ethylene-α-olefin copolymer of a relatively high molecular weight (hereinafter referred to as "copolymer A") which is used in the present invention as one mixing component, is a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms. This α-olefin is one represented by the general formula $R\text{-}CH{=}CH_2$ wherein R is an alkyl group of 1 to 16 carbon atoms. Examples of the α-olefin include propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1,4-methyl,pentene-1, 4-methyl-hexene-1 and 4,4-dimethyl-pentene-1. Among these olefins, α-olefins of at least 4 carbon atoms are preferred. Particularly, butene-1, pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1 are preferred from the standpoints of monomer availability, copolymerizability and quality of polymer obtained. These α-olefins can be used alone or in combinations of two or more. The density of the copolymer A is influenced by the kind of an α-olefin used, the content of the olefin and the intrinsic viscosity of the copolymer. For the object of this invention, the density is required to be 0.895 to 0.935 g/cm^3 and more preferably 0.895 to 0.930 g/cm^3. At a density smaller than 0.895 g/cm^3, copolymers stick to the reactor walls making polymerization difficult, or, the density of the relatively lower molecular weight copolymer (namely "copolymer B" which is described later and used as another mixing component in the present invention) is required to be raised, resulting in formation of polymer compositions of undesirable qualities such as films of poor transparency. In the density higher than 0.930 g/cm^3, the content of the α-olefin in the copolymer A becomes very low, and the copolymer A of such a high density does not give satisfactory mechanical strengths. For instance, in films, balancing of MD and TD strengths becomes difficult and heat-sealing characteristics get worse. S.C.B. in the copolymer A is 7 to 40 and preferably 10 to 40. (When R in the above α-olefin formula is a linear alkyl group, the number of methyl groups at branch ends per 1000 carbon atoms is S.C.B. When R is an alkyl group with a branch or branches, for instance, the α-olefin is 4-methyl-pentene-1, the branch is isobutyl group and the half number of methyl groups at the branch ends is S.C.B.) Short chain branching in ethylene-α-olefin copolymers occurs due to α-olefins and it hinders crystallization mainly of ethylene sequences and lowers densities. These effects vary depending upon the kind of α-olefin. Short chain branching is considered to also make some contribution to formation of interlamella molecules, and ultimately affects mechanical strengths and thermal properties of copolymers obtained. Therefore, when S.C.B. is below 7, mechanical strengths and heat-sealing properties of the composition become poor. For instance, in films, balancing of MD and TD strengths is difficult. When S. C.B. is over 40, there occur problems in polymerization of the copolymer A. Also the transparency of polymer compositions obtained from the copolymer becomes poor.

The molecular weight of the copolymer A is 1.2 to 6.0 dl/g as intrinsic viscosity and preferred to be 1.2 to 4.5 dl/g. When the intrinsic viscosity is below 1.2 dl/g, mechanical strengths of polymer compositions of the present invention are reduced. Over 6.0 dl/g, mixing with the copolymer B becomes difficult, and the polymer compositions obtained have fish eyes and further worsened flow properties as well as reduced transparency. In injection molding, the intrinsic viscosity is preferably 1.2 to 4.0 dl/g and more preferably 1.2 to 3.0 dl/g. If it is less than 1.2 dl/g, mechanical strengths of compositions are lowered. If it is over 4.0 dl/g, mixing with the copolymer B becomes insufficient, and the polymer compositions obtained have fish eyes, deteriorated flow properties (tend to cause flow marks) and reduced transparency.

(Weight average molecular weight)/(Number average molecular weight) of the copolymer A which is a measure for the molecular weight distribution of the copolymer obtained from gel permeation chromatography (hereinafter abbreviated as "GPC"), is 2 to 10 and preferably 3 to 8. If it is less than 2, such a copolymer A is difficult to produce. If it is over 10, polymer compositions have lower mechanical strengths and, when processed into films, cause blocking.

An ethylene-α-olefin copolymer of a relatively low molecular weight (hereinafter abbreviated as "copolymer B") which is used in the present invention as another mixing component, is a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms. As α-olefins, there may be selected the α-olefins used in the copolymer A. The density of the copolymer B is 0.910 to 0.955 g/cm^3. Preferably, it is 0.915 to 0.953 g/cm^3. When the density is below 0.910 g/cm^3, the copolymer compositions possess reduced mechanical strengths and cause blocking due to bleeding of lower molecular weight components of low density on film surfaces. When the density is over 0.955 g/cm^3, copolymer compositions of this invention possess worsened transparency and too high densities. In the area of injection molding, the density of the copolymer B is preferred to be 0.910 to 0.950 g/cm^3 and more preferred to be 0.915 to 0.948 g/cm^3. When the density is below 0.910 g/cm^3, mechanical strengths of compositions are reduced and surface tackiness occurs. When the density is over 0.950 g/cm^3, compositions have too high densities. S.C.B. of the copolymer B is 5 to 35 and preferred to be 7 to 30. When S.C.B. is below 5, the copolymer B has a lower molecular weight as a whole and its crystallization speed is fast, resulting in poor transparency of compositions. In case of over 35, reduction in mechanical strengths as well as blocking in films occurs.

The molecular weight of the copolymer B is 0.3 to 1.5 dl/g preferably 0.4 to 1.5 dl/g as intrinsic viscosity. When the intrinsic viscosity is less than 0.3 dl/g, mechanical strengths and transparency of compositions are reduced. In case of over 1.5 dl/g, fluidity of compositions is poor. In the area of injection molding, the molecular weight of the copolymer B is preferably 0.3 to 1.2 dl/g as intrinsic viscosity and more preferably 0.4 to 1.2 dl/g. When the intrinsic viscosity is below 0.3 dl/g, mechanical strengths and transparency of compositions are reduced. In case of over 1.2 dl/g, fluidity of compositions is poor.

The value of (weight average molecular weight)/(number average molecular weight), namely, $\overline{M}w/\overline{M}n$ of the copolymer B determined by gel permeation chromatography (GPC) is preferably 2 to 10 and more preferably 3 to 8. When $\overline{M}w/\overline{M}n$ is below 2, the copolymer B is difficult to produce. When over 10, mechanical strengths of the compositions are reduced and surface tackiness of films occurs.

The copolymer A and the copolymer B as mentioned above can be obtained by copolymerizing ethylene and an α-olefin of 3 to 18 carbon atoms under a medium to low pressure using a transition metal catalyst. For instance, catalysts such as Ziegler type catalyst and Phillips type catalyst as well as polymerization methods such as slurry polymerization, gas phase polymerization and solution polymerization are used. As catalysts, a Ziegler type catalyst system using a carrier-supported Ziegler catalyst component is convenient in this invention from its activity and copolymerizability. Specific examples of an effective carrier of this carrier-supported Ziegler catalyst component include oxides, hydroxides, chlorides and carbonates of metals and silicon and their mixtures as well as inorganic complexes. More specifically, they are magnesium oxides, titanium oxides, silica, alumina, magnesium carbonates, divalent metal hydroxychlorides, magnesium hydroxides, magnesium chlorides, magnesium alkoxides, magnesium haloalkoxides, double oxides of magnesium and aluminum and double oxides of magnesium and calcium. Among these compounds, magnesium compounds are particularly preferred. The following magnesium compounds are particularly preferred. The following magnesium compound carrier is most preferred in the production of the low density polyethylene type resin composition of this invention, because it gives a satisfactory slurry with no abnormal tackiness and there occurs no sticking of polymers to the reactor wall. (Reference is made to Japanese Patent Publication No. 23561/1980). Namely, it is the carrier obtained by (a) reacting in a solvent an aluminum halide represented by the general formula R_nAlX_{3-n} (R is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom and n is an integer of 0 to 3) and/or a silicon halide represented by the general formula R'_mSiX_{4-m} (R' is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom and m is an integer of 0 to 4) with an organomagnesium compound represented by the general formulas R"MgX and/or R''_2Mg (R" is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom), and (b) isolating the solid product formed.

As a transition metal catalyst component supported on carriers, there are, for instance, titanium compounds, vanadium compounds and zirconium compounds. Specific examples include titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, titanium trichloride, titanium alkoxy halides or titanium aryloxy halides represented by the general formula $Ti(OR^1)_{4-p}X_p$ (where R^1 is a hydrocarbon group, X is a halogen atom and p is an integer of $0<p<4$), vanadium tetrachloride, vanadium oxy trichloride, zirconium tetrachloride and zirconium alkoxy halides or zirconium aryloxy halides represented by the general formula $Zr(OR^2)_{4-q}X_q$ (where R^2 is a hydrocarbon group, X is a halogen atom and q is an integer of $0<q<4$). Among these compounds, titanium compounds and/or vanadium compounds are particularly preferred in the production of the low density polyethylene type resin composition of this invention, because they give satisfactory slurries with no abnormal tackiness and there occurs almost no sticking of polymers to the reactor wall. (Reference is made to Japanese Patent Publication No. 23561/1980). Titanium compounds are most preferred from the standpoints of weather resistance and heat resistance.

As a component of carrier-supported Ziegler catalysts used in this invention, there are also reaction products between an organomagnesium compound and a transition metal compound. Here, the transition metal compound is represented by the general formula $Ti(OR^3)_{4-r}X_r$ (where R^3 is a hydrocarbon group, X is a halogen atom and r is an integer of $0 \leqq r \leqq 4$, and includes titanium tetrahalides, titanium alkoxides, titanium aryloxides, titanium alkoxy halides and titanium aryloxy halides.

As an organometal compound component which forms the catalyst system of this invention together with the carrier-supported Ziegler catalyst component, there are organoaluminum compounds such as trialkyl aluminums (triethyl aluminum, tri-n-propyl aluminum, tri-i-butyl alminum, tri-n-butyl aluminum, tri-n-hexyl aluminum, etc.), dialkyl aluminum monohalides (diethyl aluminum monochloride, di-n-propyl aluminum monochloride, di-i-butyl aluminum monochloride, di-n-butyl aluminum monochloride, di-n-hexyl aluminum monochloride, etc.), alkyl aluminum dihalides (ethyl aluminum dichloride, n-propyl aluminum dichloride, i-butyl aluminum dichloride, n-butyl aluminum dichloride, n-hexyl aluminum dichloride, etc.), ethyl aluminum sesquichloride, i-propyl aluminum sesquichloride, i-butyl aluminum sesquichloride, n-butyl aluminum sesquichloride and n-hexyl aluminum sesquichloride as well as other organometal compounds such as organozinc compounds. These organometal compounds may be used alone or in combination of two or more.

In compounding the composition of this invention using the ethylene-α-olefin copolymer A of relatively higher molecular weight and the ethylene-α-olefin copolymer B of relatively lower molecular weight both of which are obtained with the above catalyst system under a normal medium to low pressure polymerization method, the following matters must be obeyed.

(1) From the standpoint of mechanical strengths, the copolymers A and B must be selected in order that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) becomes at least 0.6, preferably at least 0.8 and more preferably at least 1.0. Meanwhile, from the standpoint of transparency, it is necessary that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is 0.6 to 1.7. When this ratio is below 0.6, mechanical strengths of the copolymer composition obtained are reduced. In films, for instance, balancing of MD and TD strengths is difficult, heat-sealing characteristics worsen and tackiness is seen. In case of over 1.7, transparency of the copolymer composition is reduced.

(2) The density of the copolymer composition is 0.915 to 0.929 g/cm^3. When the density is below the above lower limit, mechanical strengths of the composition is reduced and, in case of films, tackiness is seen. When the density is above the upper limit, transparency of the composition worsens.

In the field of extrusion processing, the density of the copolymer composition is preferred to be 0.915 to 0.929 g/cm^3. When the density is below the lower limit, mechanical strengths of the composition is reduced and products have tackiness. When the density is above the upper limit, transparency worsens.

In the field of film processing, the density of the copolymer composition is 0.915 to 0.929 g/cm^3. When the density is below the lower limit, mechanical strengths of the composition are reduced and films possess tackiness. When the density is above the upper limit, transparency worsens.

In the field of injection molding, the density of the copolymer composition is preferred to be 0.915 to 0.929 g/cm^3. When the density is below the lower limit, mechanical strengths of the composition is reduced and molded products have tackiness. When the density is above the upper limit, transparency worsens.

(3) The melt index of the copolymer composition is 0.1 to 30 g/10 min. In addition, the melt flow ratio is 35 to 250 and preferred to be 35 to 200 and more preferred to be 35 to 150. Furthermore, the product of the melt index and the melt flow ratio is preferred to be at least 4 and more preferred to be at least 7. When the melt index and the melt flow ratio are below the lower limits, extrusion processability worsens. When they are above the upper limits, bubble stability in blown film processing is lost and mechanical strengths are reduced.

In the field of extrusion processing, the MI of the copolymer composition is preferred to be 0.10 to 2.0 g/10 min. Further, the MFR is 35 to 250 and preferred to be 35 to 200 and more preferred to be 35 to 150. Furthermore, the product of MI and MFR is preferred to be at least 4 and more preferred to be at least 7. When the MI and the MFR are below the lower limits, extrusion processability worsens. When they are above the upper limits, mechanical strengths are reduced.

In the field of film processing, the MI of the composition is preferred to be 0.1 to 3 g/10 min. Further, its MFR is 35 to 250 and preferred to be 35 to 200 and more preferred to be 35 to 150. Furthermore, the product of the MI and the MFR is preferred to be at least 4 and more preferred to be at least 7. When the MI and the MFR are below the lower limits, extrusion processability worsens. When they are above the upper limits, bubble stability in blown film processing is insufficient and mechanical strengths are reduced.

In the field of injection molding, the MI of the composition is preferred to be 2.0 to 30 g/10 min. Further, the MFR is preferred to be 35 to 80 and more preferred to be 35 to 70. When the MI is below the lower limit, moldability worsens and flow marks are produced. When it is above the upper limit, the mechanical strengths are reduced.

In order to provide the composition of this invention excellent in processability and mechanical strengths, it is also important to adequately balance its MI and MFR. A lower MI requires a higher MFR. This requirement is expressed by the product of MI and MFR. For instance, a composition having a MI of about 1 g/10 min, even if its MFR is as low as 50 to 60, has processability about equal to that of a high pressure polyethylene having the same MI. On ther other hand, a composition having a MI of about 0.05 g/10 min. and a MFR of 50 possesses extremely poor processability and, in order to have satisfactory processability, a MFR of at least 80 is required. The product of MI and MFR of a composition is designed appropriately to meet the requirement of its final application. The designed value of the product of MI and MFR can be achieved in the composition by using (a) intrinsic viscosities of the copolymer A of relatively higher molecular weight and the copolymer B of relatively lower molecular weight, (b) values of (weight average molecular weight)/(number average molecular weight) of these copolymers and (c) their mixing ratio. If intrinsic viscosities of the copolymer A and the copolymer B are put as $[\eta]_A$ (dl/g) and $[\eta]_B$ (dl/g), respectively, and their ratios by weight basis are put as W_A and W_B ($W_A+W_B=1$), respectively the intrinsic viscosity of the composition obtained by mixing the two copolymers namely $[\eta]_T$ (dl/g) is approximately given by the following formula.

$$[\eta]_T \fallingdotseq [\eta]_A W_A + [\eta]_B W_B$$

MI is governed by $[\eta]_T$ unequivocally. Meanwhile, MFR is generally larger when $[\eta]_A/[\eta]_B$ is larger, and depends upon W_A and W_B. Therefore, it is difficult to express MRF unequivocally and, based on preliminary tests, $[\eta]_A$, $[\eta]_B$, W_A and W_B are determined to give an intended MFR.

(4) In order to obtain a composition which satisfies the above (1) to (3) conditions, the copolymer A and the copolymer B are to be mixed at a ratio of 10 to 70% by weight (copolymer A) to 90 to 30% by weight (copolymer B). The ratio of 20 to 65% by weight to 80 to 35% by weight is preferred and the ratio of 30 to 60% by weight to 70 to 40% by weight is more preferred. The mixing ratio of the two copolymers must be adequately selected by considering S.C.B., densities, intrinsic viscosities and molecular weight distributions of the copolymers A and B as well as the density, MI and MFR of an intended composition. When the ratio of the copolymer A is below its lower limit and the ratio of the copolymer B is above its upper limit, the ESCR, impact strength, tear strength and low temperature resistance of the composition obtained are poor, and the high strength of the composition of this invention which is obtained when the value of (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is selected to be at least 0.6 as well as the good transparency of the composition of this invention which is obtained when the value of (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is selected to be 0.6 to 1.7, are not achieved. When the ratio of the copolymer A is above its upper limit and the ratio of the copolymer B is below its lower limit, the processability of the composition obtained worsens.

As long as the scope of this invention is obeyed, mixing of the ethylene-α-olefin copolymer A of relatively higher molecular weight and the ethylene-α-olefin copolymer B of relatively lower molecular weight is not necessarily limited to mixing one of each kind. The mixing may be also done by using two or more kinds of each of the copolymer A and the copolymer B.

There is no particular limitation to mixing methods of the copolymers A and B, and known methods can be used in mixing of these two polymers. Commonly used are a batch type melt kneading method which employs a twin roll or a Banbury mixer after separate production of the copolymers A and B, a continuous melt kneading method employing a twin rotor mixer such as CIM (manufactured by the Japan Steel Works) or FCM (manufactured by Kobe Steel) or a single screw extruder and a solution mixing method in which a mixture is obtained by dissolving the copolymers A and B in a solvent separately or together, blending and finally removing the solvent. When the copolymers A and B are produced by a high temperature solution polymerization method, it is advantageous from the process standpoint that their composition is obtained by mixing A and B in a solution state at high temperatures and removing the solvent.

Mixing by a two- or multi-stage polymerization method is also possible. In this method, in the first stage, the copolymer A is polymerized for a certain length of time and, successively in the second stage, the copolymer B is polymerized using the same catalyst but changing other polymerization conditions until the composition containing the copolymers A and B at an intended ratio is obtained. In this case, the order of polymerization of A and B is not restricted.

The above two- or multi-stage polymerization method is an ideal mixing method, because the copolymers A and B undergo molecular dispersion.

The most effective mixing method can be selected from above various mixing methods, in order to obtain a uniform composition, which meets intended requirements.

The intrinsic viscosity [η] of the ethylene-α-olefin copolymer composition of this invention is preferred to be 0.7 to 4 dl/g and more preferred to be 0.8 to 3.5 dl/g and most preferred to be 0.9 to 3 dl/g. When the intrinsic viscosity is below the lower limit, mechanical strengths are reduced and, in blown film processing, bubble stability is insufficient. In case of above the upper limit, extrusion processability worsens.

S.C.B. of the composition is 10 to 35. When S.C.B. is below its lower limit, transparency worsens. When S.C.B.

is above its upper limit, mechanical strengths are reduced and molded products have tackiness.

Next, the "index of long chain branching" of the copolymer composition of this invention is described. When the intrinsic viscosity of a copolymer composition of this invention is put as $[\eta]$ and the intrinsic viscosity of a linear polyethylene having the same $\overline{M}w$ measured by light scattering method (a high density polyethylene obtained by homopolymerization of ethylene under a medium to low pressure using a Ziegler catalyst) is put as $[\eta]_l$, $[\eta]/[\eta]_l$ namely g_η^* is called the "index of long chain branching" of the composition and indicates the extent of presence of long chain branching in the composition. Now, intrinsic viscosities of two polymers are compared. One polymer X is a polyethylene having long chain branches of which index of branching is unknown (for instance, a high pressure polyethylene) and the other polymer is a linear polyethylene containing no long chain branches but having the same $\overline{M}w$ measured by light scattering method. When these two polymers are made into respective very dilute solutions with one same solvent, the polymer X gives a less-viscous solution because the spread of its molecular chain is smaller than that of the linear polyethylene. Accordingly, by measuring the intrinsic viscosities of the two polymers and calculating their ratio namely g_η^* , the index of long chain branching can be known. When a polymer has no long chain branches, its g_η^* is almost 1 within the range of experimental errors. When the polymer has long chain branches, g_η^* is smaller than 1. In most cases, high pressure polyethylenes show g_η^* of below 0.6 and have considerable quantities of long chain branches.

The ethylene-α-olefin copolymer composition of this invention is preferred to have g_η^* of the copolymer at least 0.9 and practically has no long chain branches. When g_η^* is below 0.8 and contains a large quantity of long chain branches, the copolymer is poor in tensile strength, impact strength, environmental stress cracking resistance, low temperature resistance and chemicals resistance.

(S.C.B. of higher molecular weight components)/(S.C.B. of lower molecular weight components) of the copolymer composition of this invention is 0.6 to 0.8. Here, these S.C.B. are obtained by dividing the composition of this invention into two groups of lower molecular weight components and higher molecular weight components using molecular weight fractionation and then measuring S.C.B. of each group. When the ratio is below 0.6, mechanical strengths of the composition are poor, and when the composition is subjected to extrusion processing and injection molding, balancing of MD and TD strengths is difficult and molded products have sticky surfaces, and in films, heat-sealing characteristics worsen. When the ratio is over 0.8, transparency worsens and therefore such a polymer is not suitable for applications where transparency is required. The above molecular weight fractionation of the ethylene-α-olefin copolymer into two groups of lower and higher molecular weight components refers to the following method.

(1) A curve of molecular weight distribution is obtained by gel permeation chromatography.

In this case, the abscissa is the logarithm of chain length (unit nm) calibrated with a standard polystyrene sample, and the ordinate is relative weight fraction. The standard measurement method is described later.

(2) An example of cases where curves of molecular weight distributions have one peak was shown in Fig. 1. This pattern is seen most typically in ethylene-α-olefin copolymers. In this case, a lower molecular weight components side and a higher molecular weight components side are divided by a line drawn between the peak of the curve and the midpoint of a line drawn between the end of lower molecular weight components in the curve and the end of higher molecular weight components; and the ratio of areas of these two sides is the weight ratio of lower and higher molecular weight components. Separately, fractions of the same sample are prepared by column fractionation. These fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions become closest to the weight ratio obtained above.

(3) An example of cases where curves of molecular weight distributions have two peaks was shown in Fig. 2. Also, an example having one peak but showing a shoulder at higher molecular weight components side was shown in Fig. 3. Examples having three or more peaks are handled as modifications of two peaks and are treated similarly to two peaks. In the case of two or more peaks including shoulders, a tangent line is drawn between main two peaks of the higher molecular weight components side or between one peak and a shoulder of the same side, and then a perpendicular is drawn from a point where the distance between the GPC curve and the tangent line becomes largest. This perpendicular splits the lower molecular weight components side and the higher molecular weight components side, and the ratio of areas of these two sides becomes the weight ratio of these two components portions. When peaks are continuous and can not be detected (case of somewhat square curve), the technique of one peak distribution is applied. Separately, fraction of the same sample are prepared by column fractionation. These fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions becomes closest to the weight ratio thus obtained.

Molecular weight fractionation is conducted by the known column fractionation method. Its detailed explanation is made in "Polymer Fractionation" (compiled by M. J. R. Cantow, Academic Press, published in 1967). and therefore, only the outline of the method is described below.

About 5 g of a sample is adsorbed on a carrier, Celite® 745, in xylene and the carrier is charged into a column. The column is heated to 130°C and a mixed solvent of butyl cellosolve and xylene is passed through the column with their mixing ratio being gradually changed (namely with the solvency of the mixed solvent being gradually changed). The lower molecular weight fractions to higher molecular weight fractions are successively fractionated. To each eluate is added methanol to cause precipitation. After recovery of each polymer, they are dried under reduced pressure to be used as each fraction. To prevent the decomposition of polymers during fractionation, 100 ppm of Irganox® 1076 is added to the original sample as a stabilizer, and also nitrogen is passed through the column to shut off oxygen. The polymer fractions obtained are divided into two groups of lower and higher molecular weight components so that the weight ratio of these two groups become the above-mentioned weight ratio. Each group is made into a press sheet of about 100 to 300 μm thickness and these sheets are subjected to Fourier-transform infra-red absorption spectroscopy.

Further, it is preferable that the characteristic values of the sample obtained by dividing the ethylene-α-olefin copolymer of this invention into two fractions such as a higher molecular weight component and a lower molecular weight component are same to the characteristic values of copolymer A and copolymer B. respectively, as previously defined.

When compared with low density ethylene-α-olefin copolymers obtained from the conventional medium to low pressure method (normally called "linear low density polyethylene or LLDPE"), the polyethylene type resin composition of this invention has the following advantages.

In the field of extrusion processing, the composition of this invention is largely excellent in processability (about equal even to high pressure polyethylenes) and moreover has excellent mechanical strengths (ESCR, tensile strength, impact strength and tear strength) as well as excellent low temperature resistance. Therefore, reduction in thicknesses of molded products becomes possible. The composition of this invention has wide applications and can be used even in the application where transparency is required.

In case of films, the present composition is far superior in processability (about equal even to high pressure polyethylenes). Further, the composition has excellent mechanical strengths such as tensile strength, impact strength and tear strength, by which reduction in thicknesses of films becomes possible. Moreover, the present composition has excellent transparency and heat-sealing characteristics, by which it is used as a high quality film in wide applications including high speed bag manufacturing.

In the field of injection molding, the present composition is largely excellent in processability (about equal even to high pressure polyethylenes). Moreover, there occurs no flow marks, there is no warpage with molded products, and transparency, low temperature resistance and mechanical strengths such as environmental stress cracking resistance, tensile strength and impact strength are excellent. Thereby, reduction in thicknesses of molded products is possible and the present composition has wide applications including the case where transparency is required.

To the composition of this invention, can be added if necessary various additives being commonly used in the industries such as oxidation inhibitors, lubricants, anti-blocking agents, anti-static agents, photostabilizers, and coloring pigments. Also, other polymers can be added in small quantities as long as the scope of this invention is kept.

Next, the definitions of physical and chemical properties used in this invention are explained below.

(1) Intrinsic viscosity

This implies [η] in tetralin of 135°C.

$$[\eta]=11.65\times\log R$$

$$R=t/t_o$$

t : Seconds of dropping in a concentration of 0.2 dl/g

t_o: Seconds of dropping of tetralin itself.

(2) Density

According to the specification in JIS-K-6760.

With respect to the copolymer B of lower molecular weight, when it has a large S.C.B., it is regarded as a low density product, and according to the specification, it must be subjected to annealing of 100°C and 1 hour. However, the copolymer B was conformed in all cases to the specification for high density products and was not subjected to the above annealing.

(3) S.C.B.

Using the C_{14} labelled product described in the following literature, the subject property was calculated by employing the FT-IR spectrum substraction method.

"Characterization and Properties of Polymers", Published by Kagaku Dojin, Compiled by Mitsuru Nagasawa et al., Issued on July 10, 1970, Pages 131 to 146

Determination formulas for various branches are given below.

Branch	Determination formula
Methyl	Branches/1000 C=0.49 · K 7.25 μm
Ethyl	" =0.70 · K 7.25 μm
n-Butyl	" =0.80 · K 7.25 μm
n-Decyl	" =0.78 · K 7.25 μm
Other linear chains	" =0.80 · K 7.25 μm
i-Butyl	" =0.45 · K 7.23 μm

$K_{7.25\ \mu m}$ (absorptivity) was obtained by using as a reference a linear ethylene homopolymer having the almost same molecular weight and molecular weight distribution and the same [η] as those of a given sample and employing the spectrum substraction method. Therefore, effects of methyl groups at the ends were cleared.

When R of an α-olefin R-CH=CH_2 is a linear alkyl, (the number of methyl groups at the branch ends)/1000 C is S.C.B. When R is a branched alkyl group, for instance, an α-olefin is 4-methyl-pentene-1, the branch is the i-butyl group and half number of methyl groups at the branch ends per 1000 carbon atoms is S.C.B.

(4) Weight average molecular weight by light scattering method

This item was measured at 125°C by the normal method, with α-chloronaphthalin used as a solvent and employing a photoelectric type light scattering photometer (manufactured by Shimazu Seisakusho).

(5) Melt index (MI)

According to the condition E of ASTM D 1238.

(6) Melt flow ratio (MFR)

Firstly, $MI_{21.6}$ (grams per 10 min. under a load of 21.6 kg at 190°C) is measured according to ASTM D 1238 condition F. Then, MFR is calculated using the following formula.

$$MFR=MI_{21.6}/MI$$

(7) Rigidity (expressed by Olsen's flexural modulus)

According to ASTM D 747.

Press condition: ASTM D 1898 method C
Test piece: 25×70×1 mm thickness
Span: 25 mm
Measurement temperature: 20°C.

(8) Tensile impact strength: According to ASTM D 1822

Press condition: ASTM D 1898 method C
Test piece: S type dumbbell, 1 mm thickness
Annealing: 1 hour in boiling water
Measurement temperature: 20°C.

(9) Molecular weight distribution ($\overline{M}w/\overline{M}n$)

GPC method (gel permeation chromatography method)
HLC-811 (manufactured by Toyo Soda)
Column: TSK-Gel (GMSP+$G_{7000}H_4$+GMH×2)
Solvent: 1,2,4-trichlorobenzene (TCB)
Temperature: 145°C
Detector: Differential refractometer
Flow quantity: 1 ml/min.
Concentration: 15 mg/10 ml TCB
Measurement data on standard polystyrenes are shown below.

Polystyrene	Nominal value			Measured value		
	$\overline{M}w$	$\overline{M}n$	$\overline{M}w/\overline{M}n$	$\overline{A}w$	$\overline{A}n$	$\overline{A}w/\overline{A}n$
# 41955 (Water's)	9.82×10^4	9.62×10^4	1.02	2083	1744	1.19
A 5000 (Toyo Soda's)	62×10^3	5.96×10^3	1.04	140	112	1.25

(10) Environmental stress cracking resistance (ESCR)
According to ASTM D 1693.
Expressed in F_{50} (hr).
The following exceptions were adopted.
Concentration of Antarox®-CO630: 10% by weight
Sample: 3 mm thickness, 0.5 mm notch.

(11) Tensile strength
According to ASTM D 638.

(12) Resistance to chlorine water
Test solution: 0.2% chlorine water
Solution quantity: A quantity which gives 1.2 ml/cm^2 against a pressed sample. The solution is replaced daily.
Temperature: 40°C
Evaluation: 10 stage evaluation on a sample after 72 hours.

1: Excellent,
10: Overall surface like "foam".

(13) Transparency (haze value)
Press condition: 180°C×10 min, rapid cooling in ice water
Sample: 100 µm thickness
Haze measurement: Internal haza.

(14) Brabender torque
Brabender plastograph® was used.
Jacket: W 50 model, 45 g filled
Temperature: 190°C
Rotor revolution: 60 rpm
A torque after 30 min. is expressed in kg-m.

(15) Spiral flow length
Injection molding machine: 141,7 g injection molding machine manufactured by the Japan Steel Works, Ltd.

Mold: Spiral mold (7.5 mmϕ semicircle, 2000 mm length)
Molding condition: Resin temperature 250°C
Mold temperature 40°C
Injection pressure 840 bar.

Injection molding is carried out with this molding condition and spiral flow length is measured.

The present invention is explained below in more detail by the following examples, but it is not restricted by these examples.

Reference Example 1

(1) Synthesis of Organomagnesium compound

In a 500 ml four-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel was placed 16.0 g of flake-shaped magnesium to be used for the production of Grignard reagents. The air and moisture inside the flask were completely replaced by nitrogen. Into the dropping funnel were charged 68 ml (0.65 mol) of n-butyl chloride and 30 ml of n-butyl ether. About 30 ml of this solution was dropped into the flask to initiate a reaction, and thereafter the rest of the solution was dropped in 4 hours at 50°C. After the completion of dropping, the reaction was continued for further 1.5 hours at 60°C. Then, the reaction system was cooled to room temperature and the unreacted magnesium was filtered off by the use of a glass filter.

n-Butyl magnesium chloride in the n-butyl ether was measured for its concentration by hydrolyzing with 1 N sulfuric acid and back-titrating with 1 N sodium hydroxide using phenolphthalein as an indicator. The concentration was 1.96 mol/l.

(2) Synthesis of solid catalyst component

The air and moisture inside a 500 ml four-necked flask equipped with a stirrer, a dropping funnel and a thermometer was completely replaced by nitrogen. In the flask was placed 130 ml of the n-butyl ether solution containing 0.26 mol of n-butyl magnesium chloride synthesized in the above step (1). From the dropping funnel was dropped 30 ml (0.26 mol) of silicon tetrachloride over 2 hours at 50°C. The reaction was continued further 1 hour at 60°C. The formed white solid was separated. washed with n-heptane and dried under reduced pressure to obtain 31.5 g of a white solid. Ten grams of this white solid was placed in a 100 ml four-necked flask and 50 ml of titanium tetrachloride was added. They were allowed to react with stirring for 1 hour at 100°C. After the completion of the reaction, n-heptan washing was applied until the washings became free from titanium tetrachloride. After drying under reduced pressure, 7.9 g of a solid catalyst component was obtained. Each 1 g of this solid catalyst component supported 14 mg of titanium.

Reference Example 2

Ethylene-α-olefin copolymers A were polymerized, using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions as shown in Table 1. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these polymers obtained were also shown in Table 1.

These copolymers are used in the following examples as mixing components.

Reference Example 3

Ethylene-α-olefin copolymers B were polymerized, using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions as shown in Table 2. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene-α-olefin copolymers were also shown in Table 2.

These copolymers are used in following examples as mixing components.

TABLE 1

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{M}w/\overline{M}n$
A1-1	Slurry	65	134	TEA 100	C_4 6.0	C_4' 6.14	0.84	5.6	50	0.900	2.2	38	5.9
A1-2	Solution	1	25.3	DEAC 2.5	C_7 0.25	4-MP-1 0.110	0.1	20	140	0.904	2.5	23	3.6
A1-3	Slurry	65	130	TEA 50	C_4 6.0	C_4' 6.14	0.25	6.0	50	0.905	3.2	30	5.8
A1-4	"	65	310	TEA 100	"	"	0.86	9.5	50	0.915	2.5	19	5.5
A1-5	"	65	102	TEA 50	"	"	0.059	4.5	50	0.908	4.4	25	6.0
A1-6	Solution	1	26.0	DEAC 2.5	C_7 0.30	C_6' 0.060	0.1	20	140	0.903	2.5	25	3.7
A1-7	"	1	327	TEA 100	"	"	1.8	12.0	140	0.922	2.2	13	5.3
A1-8	"	1	24.5	DEAC 2.5	"	4-MP-1 0.050	0.15	20	140	0.920	2.5	10	3.7
A1-9	Slurry	65	330	TEA 100	C_4 6.0	C_4' 6.14	1.1	12.0	50	0.921	2.5	13	5.5
A1-10	"	65	309	TEA 100	"	"	1.2	8.0	50	0.911	2.2	25	5.7
A1-11	"	65	121	TEA 50	"	"	0.98	6.5	50	0.907	2.2	30	5.7
A1-12	"	65	320	TEA 100	"	"	3.0	20	50	0.928	2.2	8	5.3
A1-13	Solution	1	25.0	DEAC 2.5	C_7 0.25	C_8 0.140	0.1	20	140	0.903	2.5	24	3.9

Note:

TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1: 4-Methylpentene-1
C_2 = Ethylene
C_4 = n-Butane
C_4 = Butene-1
C_6' = Hexene-1
C_8' = Octene-1
C_7 = n-Heptane

TABLE 2

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{M}w/\overline{M}n$
B1-1	Slurry	65	345	TEA 100	C_4 15.2	C_4' 1.2	11.5	5.0	70	0.943	0.63	15	5.5
B1-2	Solution	1	25.5	DEAC 2.5	C_7 0.28	4-MP-1 0.030	3.0	10	140	0.938	0.50	13	3.5
B1-3	Slurry	65	415	TEA 50	C_4 15.2	C_4' 1.6	11.0	5.0	70	0.936	0.62	20	5.6
B1-4	..	65	425	..	..	C_4' 2.0	10.5	5.0	70	0.929	0.65	25	5.7
B1-5	..	65	286	..	C_4 6.0	C_4' 6.14	9.4	8.5	50	0.927	1.1	25	5.8
B1-6	..	65	410	TEA 100	C_4 12.0	C_4' 3.0	11.0	3.0	50	0.910	0.60	35	5.9
B1-7	Solution	1	25.7	DEAC 2.5	C_7 0.25	4-MP-1 0.050	2.5	10	140	0.912	0.52	22	3.6
B1-8	Slurry	65	250	TEA 100	C_4 15.2	C_4' 0.4	13.5	1.5	50	0.930	0.28	25	5.7
B1-9	..	65	407	..	..	C_4' 0.5	13.0	5.0	70	0.954	0.62	8	5.2
B1-10	..	65	422	TEA 50	..	C_4' 1.8	11.0	5.0	70	0.934	0.61	22	5.6
B1-11	..	65	405	..	..	C_4' 1.4	11.0	5.0	70	0.939	0.62	18	5.5
B1-12	Solution	1	26	DEAC 2.5	C_7 0.25	C_8' 0.040	3.0	10	140	0.937	0.49	14	3.6

Note:
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_2' = Ethylene
C_4 = n-Butane
C_4' = Butene-1
C_6' = Hexane-1
C_8' = Octene-1
C_7 = n-Heptane.

Reference Example 4

Ethylene-α-olefin copolymers A were polymerized, using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions shown in Table 3. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/α-olefin copolymers were also shown in Table 3.

These copolymers are used in the following examples as mixing components.

Reference Example 5

Ethylene-α-olefin copolymers B were polymerized, using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions as shown in Table 4. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/α-olefin copolymers were also shown in Table 4.

These copolymers are used in the following examples as mixing components.

TABLE 3

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{M}w/\overline{M}n$
A2-1	Slurry	65	145	TEA 100	C_4 6.0	C_4' 6.14	1.38	6.0	50	0.902	1.8	38	5.9
A2-2	Solution	1	25.5	DEAC 2.5	C_7 0.25	4-MP-1 0.11	0.5	20	140	0.908	1.8	23	3.8
A2-3	Slurry	65	141	TEA 50	C_4 6.0	C_4' 6.14	0.59	6.5	50	0.907	2.5	30	5.8
A2-4	"	65	307	TEA 100	"	"	2.3	11	50	0.918	1.8	17	5.4
A2-5	"	65	311	"	"	"	1.84	8.4	50	0.914	1.8	25	5.7
A2-6	"	65	321	"	"	"	3.2	14	50	0.925	1.8	13	5.3
A2-7	Solution	1	26.5	DEAC 2.5	C_7 0.3	4-MP-1 0.05	0.9	20	140	0.923	1.8	10	3.6
A2-8	Slurry	65	315	TEA 100	C_4 6.0	C_4' 6.14	2.6	8.5	50	0.914	1.6	25	5.5
A2-9	"	65	118	"	"	"	4.6	17	50	0.929	1.6	10	5.3
A2-10	Solution	1	24.5	DEAC 2.5	C_7 0.3	C_6' 0.025	0.9	20	140	0.918	1.8	13	3.8

Note:

TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_2' = Ethylene
C_4 = n-Butane
C_4' = Butene-1
C_6' = Hexene-1
C_7 = n-Heptane.

TABLE 4

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{M}w/\overline{M}n$
B2-1	Slurry	65	348	TEA 100	C_4 15.2	C_4' 1.0	12	3.0	70	0.943	0.51	15	5.9
B2-2	Solution	1	26.5	DEAC 2.5	C_7 0.28	4-MP-1 0.03	3.0	10	140	0.938	0.50	13	3.5
B2-3	Slurry	65	405	TEA 50	C_4 15.2	C_4' 1.6	8.8	5.0	70	0.935	0.73	20	5.9
B2-4	"	65	421	"	"	"	12	3.0	70	0.929	0.54	25	5.9
B2-5	"	65	407	TEA 100	C_4 12.0	C_4' 2.5	12	3.0	50	0.910	0.51	35	6.0
B2-6	Solution	1	25.7	DEAC 2.5	C_7 0.25	4-MP-1 0.05	2.5	10	140	0.912	0.52	22	3.6
B2-7	Slurry	65	245	"	C_4 15.2	C_4' 0.3	12	1.0	50	0.931	0.25	25	5.9
B2-8	"	65	420	TEA 50	"	C_4' 1.2	12	3.0	70	0.938	0.50	18	5.4
B2-9	Solution	1	23.9	DEAC 2.5	C_7 0.30	C_6' 0.017	3.0	10	140	0.937	0.52	18	3.4

Note:

TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-methylpentene-1
C_2' = Ethylene
C_4 = n-Butane
C_4' = Butene-1
C_6' = Hexene-1
C_7 = n-Heptane.

The below-described are mixing methods of an ethylene-α-olefin copolymer A having a relatively higher molecular weight and an ethylene-α-olefin copolymer B having a relatively lower molecular weight.

(a) Mixing with a Banbury mixer (hereinafter referred to as Banbury mixing)

A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 1.0 kg. The mixture is kneaded in a Banbury mixer for 5 min. with a rotor revolution of 150 to 230 rpm. At that time, nitrogen replacement should be made sufficiently and the polymer temperature must not exceed 250°C.

(b) Mixing in a solution state (hereinafter referred to as solution mixing)

A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 100 g. This mixture is charged into a 3 liter autoclave. Two liters of xylene is added as a solvent. With stirring, the mixture is heated up to 200°C and is subjected to 1 hour of solution mixing. Then, it is cooled below the boiling point, and is added into 10 liters of methanol to cause precipitation. The precipitate is dried for 48 hours in a vacuum drier of 80°C to obtain an intended polymer composition.

Reference Example 6

Ethylene-α-olefin copolymers A were polymerized using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 5. Their densities. intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) are shown in Table 5.

These polymers are used in the following Examples as mixing components.

TABLE 5

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{M}w/\overline{M}n$
A3-1	Slurry	65	131	TEA 100	C_4 6.0	C_4' 6.14	0.45	5.0	50	0.899	2.6	38	5.9
A3-2	Solution	1	25.1	DEAC 2.5	C_7 0.22	4-MP-1 0.130	0.10	20	140	0.899	2.6	27	3.5
A3-3	"	1	24.8	"	C_7 0.30	C_6' 0.055	0.10	20	140	0.902	2.6	24	3.7
A3-4	Slurry	65	307	TEA 100	C_4 6.0	C_4' 6.14	0.9	9.0	50	0.914	2.4	22	6.0
A3-5	"	65	130	TEA 50	"	"	0.22	5.5	50	0.906	3.2	28	5.8
A3-6	"	65	125	"	"	"	1.8	18	50	0.923	2.6	9	5.5
A3-7	"	65	301	TEA 100	"	"	1.2	12	50	0.919	2.4	16	5.8
A3-8	"	65	318	"	"	"	2.0	20	50	0.928	2.4	8	5.4
A3-9	"	65	308	"	"	"	1.4	9.0	50	0.914	2.2	22	5.7

Note

TEA triethyl aluminum
4-MP-1 4-Methylpentene-1
C_4' Butene-1
DEAC Diethyl aluminum chloride
C_2' Ethylene
C_6' Hexene-1
C_4 n-Butane
C_7 n-Heptane

Reference Example 7

Ethylene-α-olefin copolymers B were polymerized using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions shown in Table 6. Their densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) are shown in Table 6.

These copolymers are used in the following Examples as mixing components.

TABLE 6

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\bar{M}w/\bar{M}n$
B3-1	Slurry	65	405	TEA 50	C_4 12.0	C_4' 2.0	10.8	8.3	70	0.942	0.83	15	5.5
B3-2	Solution	1	25.5	DEAC 2.5	C_7 0.30	4-MP-1 0.025	2.4	10	140	0.943	0.81	10	3.7
B3-3	„	1	24.2	„	C_7 0.32	C_6' 0.013	2.4	10	140	0.940	0.82	12	3.8
B3-4	Slurry	65	330	TEA 100	C_4 15.2	C_4' 0.7	7.5	5.0	70	0.949	0.75	11	5.3
B3-5	„	65	391	„	„	C_4' 1.8	7.2	8.0	70	0.941	0.92	14	5.4
B3-6	„	65	408	„	C_4 12.0	C_4' 4.0	5.2	4.0	50	0.910	0.82	35	5.9
B3-7	„	65	350	„	C_4 15.2	C_4' 1.3	7.5	5.0	70	0.942	0.75	16	5.8
B3-8	„	65	405	TEA 50	„	C_4' 1.6	8.8	5.0	70	0.935	0.74	20	5.9
B3-9	„	65	390	TEA 100	„	C_4' 0.20	15.0	1.5	70	0.949	0.27	11	5.6

Note

TEA - triethyl aluminum
4-MP-1 - 4-Methylpentene-1
C_4' = Butene-1
DEAC - Diethyl aluminum chloride
C_2' - Ethylene
C_6' = Hexene-1
C_4 = n-Butane
C_7 - n-Heptane

Reference Example 28

Ethylene-α-olefin copolymers A were synthesized using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 7. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers are shown in Table 7.

These copolymers are used in the following examples as mixing components.

Reference Example 9

Ethylene-α-olefin copolymers B were synthesized using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 8. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers are shown in Table 8.

These copolymers are used in the following examples as mixing components.

TABLE 7

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'- partial pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\bar{M}w/\bar{M}n$
A4-1	Slurry	65	310	TEA 100	C_4 6.0	C_4' 6.14	0.70	7.8	50	0.912	2.6	24	5.6
A4-2	Solution	1	24.3	DEAC 2.5	C_7 0.27	4-MP-1 0.090	0.15	20	140	0.912	2.5	17	3.4
A4-3	Slurry	65	83	TEA 50	C_4 6.0	C_4' 6.14	0.09	7.0	50	0.912	4.4	20	5.8
A4-4	"	65	309	TEA 100	"	"	1.2	3.0	50	0.911	2.2	25	5.7
A4-5	"	65	145	TEA 50	"	"	0.59	6.7	50	0.906	2.6	29	5.8
A4-6	Solution	1	25.2	DEAC 2.5	C_7 0.30	C_6' 0.035	0.2	20	140	0.909	2.2	18	3.4
A4-7	Slurry	65	303	TEA 100	C_4 6.0	C_4' 6.14	0.36	9.0	50	0.917	3.3	16	5.6
A4-8	"	65	125	"	"	"	1.8	18	50	0.923	2.6	9	5.5
A4-9	Solution	1	24.5	DEAC 2.5	C_7 0.40	4-MP-1 0.040	0.25	20	140	0.923	2.5	8	3.3
A4-10	Slurry	65	121	TEA 100	C_4 6.0	C_4' 3.7	1.2	20	50	0.925	3.3	6	5.5
A4-11	"	65	302	"	"	C_4' 6.14	1.4	8.5	50	0.913	2.1	23	5.4

Note

TEA Triethyl aluminum
DEAC Diethyl aluminum chloride
4 MP 1 4 Methylpentene 1
C_4 n Butane
C_4' Butene-1
C_6' Hexene-1
C_7 n Heptane

TABLE 8

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties			
										Density (g/cm³)	[η] (dl/g)	S.C.B.	$\bar{M}w/\bar{M}n$
B4-1	Slurry	65	402	TEA 50	C_4 12.0	C_4' 3.2	7.8	7.6	70	0.929	0.85	24	5.8
B4-2	Solution	1	24.2	DEAC 2.5	C_7 0.80	4-MP-1 0.045	2.2	10	140	0.929	0.81	17	3.6
B4-3	Slurry	65	405	TEA 50	C_4 12.0	C_4' 3.2	7.0	6	70	0.928	0.90	24	5.7
B4-4	..	65	425	..	C_4 15.2	C_4' 2.0	10.5	5	70	0.929	0.65	25	5.7
B4-5	..	65	411	..	..	C_4' 1.6	6.5	5	70	0.935	0.83	20	5.5
B4-6	Solution	1	25.1	DEAC 2.5	C_7 0.82	C_6' 0.017	2.7	10	140	0.926	0.63	18	3.5
B4-7	Slurry	65	346	TEA 100	C_4 15.2	C_4' 1.1	12	3	70	0.941	0.52	16	5.4
B4-8	..	65	408	..	C_4 12.0	C_4' 4.0	5.2	4	50	0.910	0.82	35	5.9
B4-9	Solution	1	24.9	DEAC 2.5	C_7 0.28	4-MP-1 0.055	2.0	10	140	0.912	0.85	22	3.7
B4-10	Slurry	65	250	TEA 100	C_4 15.2	C_4' 0.4	13.5	1.5	50	0.930	0.28	25	5.7
B4-11	..	65	410	TEA 50	..	C_4' 1.4	12	3	70	0.934	0.53	22	5.8
B4-12	..	65	290	..	C_4 6.0	C_4' 6.14	8.1	9	50	0.927	1.2	23	5.7

Note

TEA: Triethyl aluminum
DEAC: Diethyl aluminum chloride
4-MP-1: 4-Methylpentene-1
C_4: n-Butane
C_4': Butene-1
C_6': Hexene-1
C_7: n-Heptane

Example 1

Ethylene-α-olefin copolymers were synthesized using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 9. Densities, intrinsic viscosities, and S.C.B. of these copolymers are shown in Table 9.

These copolymers are used in the following Examples as higher molecular weight components.

Example 2

Ethylene-α-olefin copolymers were synthesized using the catalyst produced in Reference Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 10. Densities, intrinsic viscosities and S.C.B. of these copolymers are shown in Table 10.

These copolymers are used in the following Examples as lower molecular weight components.

TABLE 9

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties		
										Density (g/cm³)	[η] (dl/g)	S.C.B.
A-1	Slurry	65	131	TEA 100	C_4 6.0	C_4' 6.14	0.45	5.0	50	0.899	2.6	38
A-2	,,	65	145	TEA 50	,,	,,	0.59	6.7	50	0.906	2.6	29
A-3	,,	65	310	TEA 100	,,	,,	0.70	7.8	50	0.912	2.6	24
A-4	,,	65	125	,,	,,	,,	1.8	18	50	0.923	2.6	9
A-5	Solution	1	25.3	DEAC 2.5	C_7 0.25	4 MP-1 0.11	0.1	20	140	0.904	2.5	23
A-6	,,	1	24.5	,,	C_7 0.30	4 MP-1 0.05	0.15	20	140	0.920	2.5	10
A-7	Slurry	65	121	TEA 50	C_4 6.0	C_4' 6.14	0.98	6.5	50	0.907	2.2	30
A-8	,,	65	320	TEA 100	,,	,,	3.0	20	50	0.928	2.2	8

Note

TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_4 = n-Butane
C_4' = Butene-1
C_7 = n-Heptane

TABLE 10

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2'-partial pressure (bar)	Polymerization temperature (°C)	Properties		
										Density (g/cm^3)	[η] (dl/g)	S.C.B.
B-1	Slurry	65	405	TEA 50	C_4 50	C_4' 2.0	10.8	8.3	70	0.912	0.83	15
B-2	,,	65	411	,,	C_4 15.2	C_4' 1.6	6.5	5	70	0.935	0.83	20
B-3	,,	65	402	,,	C_4 12.0	C_4' 3.2	7.8	6	70	0.929	0.85	24
B-4	,,	65	408	TEA 100	,,	C_4' 4.0	5.2	4	50	0.910	0.82	35
B-5	Solution	1	26.5	DEAC 2.5	C_7 0.28	4-MP-1 0.03	3.0	10	140	0.938	0.50	13
B-6	,,	1	25.7	,,	C_7 0.25	4-MP-1 0.05	2.5	10	140	0.912	0.52	22
B-7	Slurry	65	407	TEA 100	C_4 15.4	C_4' 0.5	13.0	5	70	0.953	0.62	9
B-8	,,	65	422	TEA 50	C_4 15.2	C_4' 1.8	11.0	5	70	0.934	0.61	22

Note

TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_4 = n-Butane
C_4' = Butene-1
C_7 = n-Heptane

Example 3

A composition of ethylene-α-olefin copolymers was prepared in two stage polymerization. The first stage polymerization was carried out for 70 min. using the catalyst produced in Reference Example 1 and triethyl aluminum (cocatalyst) and other polymerization conditions as shown in Table 11. Successively, the second stage polymerization was conducted for 180 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 11. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen was kept constant at respective fixed levels. The polymerized quantities in each stage were calculated from the quantities of fed ethylene. The copolymer composition consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer was taken out and measured for its density, intrinsic viscosity and S.C.B. The whole polymer obtained after the second stage was also measured for the same test items. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and the number of branched short chains of the polymer formed in the second stage alone were calculated. These values were shown in Table 11. The whole polymer gave: density 0.921 g/cm^3, MI 0.5 g/10 min., MFR 70, intrinsic viscosity 1.7 dl/g, S.C.B. 24, g_η^* 0.93. The whole polymer was subjected to gel permeation chromatography and a curve of molecular weight distribution shown in Fig. 4 was obtained.

Because of bimodal distribution which has two peaks, the curve was divided into two parts using broken lines. The areas of each part were calculated, and the lower molecular weight components and the higher molecular weight components were determined to be 48 and 52% by weight, respectively.

The whole polymer was divided into 30 fractions using column chromatography. These fractions were divided into two parts (the lower molecular weight components and the higher molecular weight components) so that the former became 48% by weight and the latter 52% by weight. S.C.B., densities and intrinsic viscosities of each component are shown in Table 13.

Flow characteristics and solid physical properties of the whole polymer are shown in Table 14.

In the following examples, ethylene-α-olefin copolymers as higher molecular weight components and ethylene-α-olefin copolymers as lower molecular weight components were mixed at respective fixed ratios (total quantity 1 kg) and kneaded for 5 min. with a Banbury mixer (150 to 230 rpm). At that time, replacement by nitrogen was conducted completely and the polymer temperatures were controlled not to exceed 250°C.

When sample quantities were small, mixing was made in xylene. After mixing, the whole solution was added into methanol to cause precipitation. After filtration, the precipitate was completely dried in a vacuum drier and used as a copolymers composition sample.

Examples 4, 5

Ethylene-α-olefin copolymers obtained in Example 1 and ethylene-α-olefin copolymers obtained in Example 2 were kneaded with a Banbury mixer at ratios as shown in Table 12.

Thus, compositions of copolymers having densities. MIs, MFRs. intrinsic viscosities, S.C.B. and g_η^* shown in Table 13 were obtained. These compositions had molecular weight distribution curves about equal to Fig. 4. With the same technique as used in Example 3, quantities of lower molecular weight components and higher molecular weight components were calculated, and they were both approximately 50% by weight as shown in Table 13. Physical properties of these compositions are shown in Table 14.

With the same technique as used in Example 3, column fractionation was applied in order to divide into higher molecular weight components and lower molecular weight components. Characteristics of the components are shown in Table 13.

In Tables 13 and 14 are also shown Example 3 using a composition of ethylene-α-olefin copolymers prepared in two stage polymerization and, for comparison, Comparative Example 1 using a high pressure method polyethylene of the conventional technique (commercial product Sumikathene® F 101-1 manufactured by Sumitomo Chemical Co., Ltd.), Comparative Example 2 using a composition of low density ethylene-α-olefin copolymers of the conventional technique and Comparative Example 3 using a composition of low density ethylene-α-olefin copolymers of the conventional technique of which molecular weight distribution is made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

As is obvious from Tables 13 and 14, when compared with the high pressure polyethylene, the copolymer compositions of this invention have about equivalent Brabender torques (excellent in processability), and are largely excellent in tensile impact strength, rigidity, ESCR and tensile strength. Transparency is equally good, because distribution index of S.C.B. is in a certain range as defined by the present invention. When compared with the composition of low density ethylene-α-olefin copolymers of the conventional technique, the compositions of this invention have far smaller Brabender torques (much better processability) and higher tensile impact strengths and tensile strengths.

From comparison between Comparative Examples 2 and 3 in Tables 13 and 14, it is learned that widening of molecular weight distribution (larger MFR gives wider distribution) in the manufacture of a low density ethylene-α-olefin copolymer of the conventional technique with density and MI fixed results in large reduction in tensile impact strength and tensile strength.

TABLE 11

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (g)	α olefin (g)	H_2 partial pressure (bar)	C_2'- partial pressure (bar)	Polymerization temperature (°C)	Polymerization time (min)	Properties		
											Density (g/cm³)	[η] (dl/g)	S.C.B.
1st stage	Slurry	5	24.3	5	C_4 1000	C_4' 250	0.6	4	50	70	0.912	2.6	24
2nd stage	Slurry						10	5		180	—	(0.8)	(23)

Note
C_4 n-Butane
C_4' = Butene-1
C_2' = Ethylene
TEA Triethyl aluminum
( ) Calculated values

TABLE 12

	Higher molecular weight component		Lower molecular weight component	
	Designation	% by weight	Designation	% by weight
Example 4	A 2	50	B-2	50
Example 5	A 3	50	B-3	50
Comparative Example 3	A 4	50	B-4	50

TABLE 13

	Properties of copolymer						GPC			
							Length of main peak chain (nm)		Ratio (% by weight)	
	Density (g/cm^3)	MI (g/10 min.)	MFR	[η] (dl/g)	S.C.B.	g^*_η	Lower molecular weight component	Higher molecular weight component	Lower molecular weight component	Higher molecular weight component
Example 3	0.921	0.5	70	1.7	24	0.96	1.7×10^2	3.4×10^2	48	52
Example 4	0.920	0.5	70	1.7	25	0.93	1.6×10^2	3.5×10^2	47	53
Example 5	0.920	0.5	70	1.7	24	0.97	1.9×10^2	3.4×10^2	48	52
Comparative Example 1	0.922	0.3	65	1.06	23	0.48	1.05×10^2	6.5×10^2	36	64
Comparative Example 2	0.920	0.5	30	1.7	23	0.95	Uniform distribution (peak) 2.8×10^2		50	50
Comparative Example 3	0.920	0.5	70	1.7	22	0.95	1.6×10^2	3.6×10^2	49	51

$$^*\text{Distribution index of S.C.B.} = \frac{\text{Degree of S.C.B. of higher molecular weight component}}{\text{Degree of S.C.B. of lower molecular weight component}}$$

TABLE 13 (Cont'd)

Characteristics of components fractionated by column fractionation						
Lower molecular weight component			Higher molecular weight component			
S.C.B.	Density (g/cm^3)	[η] (dl/g)	S.C.B.	Density (g/cm^3)	[η] (dl/g)	Distribution index of S.C.B.*
30	0.920	0.8	18	0.915	2.6	0.6
28	0.923	0.7	20	0.914	2.5	0.7
30	0.920	0.8	18	0.915	2.5	0.6
27	0.916	0.6	19	0.926	1.4	0.7
38	0.906	1.1	8	0.925	2.4	0.2
37	0.907	0.8	7	0.926	2.6	0.2

TABLE 14

	Physical properties of copolymer						
	Tensile impact strength (9.81 Ncm/cm^2)	Olsen's flexural modulus (9.81 N/cm^2)	Tensile strength (9.81 N/cm^2)	Haze (%)	Torque (9.81 N/m)	ESCR F_{50} (hr)	Tackiness
Example	340	2800	280	5	2.0	>1000	o
Example	400	2700	300	8	2.0	>1000	o
Example 5	350	2800	280	5	2.0	>1000	o
Comparative Example 1	200	2200	180	6	2.2	30	o
Comparative Example 2	280	3200	260	8	3.5	>1000	o
Comparative Example 3	150	3300	210	12	2.0	>1000	x

Example 6

A composition of ethylene-α-olefin copolymers was prepared by mixing an ethylene-α-olefin copolymer obtained in Example 1 and an ethylene-α-olefin copolymer obtained in Example 2 at a ratio shown in Table 15. Densities, MIs, MFRs, [η], S.C.B. and g^*_η of this composition is shown in Table 16. The physical properties are shown in Table 17.

The molecular weight distribution of Example 6 showed "one almost symmetrical mountain" curve. Column fractionation was applied with the same technique as used in Example 3. Its result is shown in Table 16.

In Tables 16 and 17 are also shown low density ethylene-α-olefin copolymers of the conventional technique (Comparative Examples 4 and 5) of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

Curves of molecular weight distributions of Comparative Examples 4 and 5 were similar to that of Example 6. As seen from Tables 16 and 17, in the composition of this invention, S.C.B. of higher molecular weight components and those of lower molecular weight components are nearly equal (compare Example 6 with Comparative Example 4.), therefore, the composition of the present invention is far superior to the copolymers of the conventional technique in tensile impact strength and tensile strength.

Comparative Example 1

A commercial high pressure polyethylene (Sumikathene® F 101-1 manufactured by Sumitomo Chemical Co., Ltd.) was subjected to measurements of physical properties and. Results are shown in Table 14.

This polyethylene has low g^*_η of 0.48 and it suggests that this sample has many long chain branches. Its molecular weight distribution curve was shown in Fig. 5. Column fractionation was applied with the same technique as used in Example 12. The fractions obtained were divided into two groups so that the lower molecular weight component group and the higher molecular weight component group became about 36 and 64% by weight, respectively. Densities, S.C.B. and intrinsic viscosity of each group are measured and results are shown in Table 13.

Comparative Example 2

A low density ethylene-α-olefin copolymer of the conventional technique was synthesized using the catalyst produced in Reference Example 1, triethyl aluminum (co-catalyst) and other polymerization conditions as shown in Table 18. The copolymer gave: density 0.920 g/cm^3. MI 0.5 g/10 min., MFR 30, intrinsic viscosity 1.7 dl/g, S.C.B. 23, g^*_η 0.95. Its physical properties are shown in Table 14. Its molecular weight distribution showed "one almost symmetrical mountain" curve, as seen in Fig. 1. From the area ratio, the lower molecular weight components and the higher molecular weight components were determined to be both 50% by weight. Column fractionation was applied with the same technique as used in Example 12 and results are shown in Table 13.

Comparative Example 3

By mixing the ethylene-α-olefin copolymer A-4 obtained in Example 1 and the ethylene-α-olefin copolymer B-4 obtained in Example 2 at the ratio as given in Table 12, a composition of low density ethylene-α-olefin copolymers of the conventional technique was prepared of which molecular weight distribution is made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Its density, MI, MFR, [η], and g^*_η are shown in Table 13. The molecular weight distribution curve of this composition was almost equal to that in Fig. 4. With the same technique as used in Example 3, the ratio of the lower and higher molecular weight components was determined. Column fractionation was also conducted. These results are shown in Table 13. Physical properties of this composition are shown in Table 14.

Comparative Examples 4, 5

By mixing ethylene-α-olefin copolymers obtained in Example 1 and ethylene-α-olefin copolymers obtained in Example 2 at ratios as shown in Table 15, compositions of low density ethylene-α-olefin copolymers of the conventional technique were prepared of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs, [η], S.C.B. and g^*_η of these compositions were shown in Tables 16. Physical properties of these compositions are shown in Table 17.

TABLE 15

	Higher molecular weight component		Lower molecular weight component	
	Designation	% by weight	Designation	% by weight
Example 6	A-5	60	B-5	40
Comparative Example 4	A-6	60	B-6	40
Comparative Example 5	A-8	50	B-8	50

TABLE 16

	Properties of copolymer						GPC			
							Length of main peak chain (nm)		Ratio (% by weight)	
	Density (g/cm^3)	MI (g/10 min)	MFR	[η] (dl/g)	S.C.B.	g_η^*	Lower molecular weight component	Higher molecular weight component	Lower molecular weight component	Higher molecular weight component
Example 6	0.920	0.5	70	1.7	19	0.91	Uniform distribution (peak) 2.5×10^2		57	43
Comparative Example 4	0.919	0.5	70	1.7	17	0.96	Uniform distribution (peak) 2.5×10^2		58	42
Comparative Example 5	0.929	1.2	70	1.4	17	0.93	Uniform distribution (peak) 1.6×10^2		48	52

$$^*\text{Distribution index of S.C.B.} = \frac{\text{Degree of S.C.B. of higher molecular weight component}}{\text{Degree of S.C.B. of lower molecular weight component}}$$

TABLE 16 (Cont'd)

Characteristics of components fractionated by column fractionation						
Lower molecular weight component			Higher molecular weight component			Distribution index of S.C.B.*
S.C.B.	Density (g/cm^3)	[η] (dl/g)	S.C.B.	Density (g/cm^3)	[η] (dl/g)	
22	0.933	0.5	15	0.920	2.4	0.7
24	0.930	0.5	7	0.927	2.4	0.3
29	0.922	0.6	6	0.930	2.1	0.2

TABLE 17

	Physical properties of copolymer			
	Tensile impact strength (9.81Ncm/cm^2)	Olsen's flexural modulus (9.81N/cm^2)	Tensile strength (9.81N/cm^2)	Tackiness
Example 6	480	2600	320	o
Comparative Example 4	200	3100	200	x
Comparative Example 5	70	4500	200	o

TABLE 18

Poly-meri-zation method	Poly-meri-zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Sol-vent (kg)	α-olefin (kg)	H_2 partial pressure (bar)	C_2' partial pressure (bar)	Polymeri-zation tempera-ture (°C)	Polymeri-zation time (min)
Slurry	65	202	100	C_4 7.0	C_4' 7.16	3.0	10	50	90

Note

TEA=Triethyl aluminum

C_4=n-Butane

C_2'=Ethylene

C_4'=Butene-1

TABLE 19

Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Solvent (g)	α-olefin (g)	H_2 partial pressure (kg/cm^2)	C_2' partial pressure (kg/cm^2)	Polymerization temperature (°C)	Polymerization time (min)
Solution	1	25.1	C_7 300	C_4' 40	3.5	20	140	90

TABLE 20

Properties			
Density (g/cm^3)	MI (g/10 min)	MFR	S.C.B.
0.924	4	25	20

Reference Example 10

An ethylene-α-olefin copolymer was synthesized from ethylene and butene-1, using the catalyst produced in Reference Example 1, diethyl aluminum monochloride (co-catalyst) and other polymerization conditions as shown in Table 19. Properties of this copolymer are shown in Table 20. By applying column fractionation, the copolymer was fractionated into fractions of different molecular weights. Then, distribution of S.C.B. against molecular weight was examined as shown in Fig. 7.

In column fractionation, about 5 g of the sample was placed in a fractionation column after being adsorbed on a carrier (Celite® 745) in xylene. Then, the column was heated to 130°C, and butyl cellosolve and xylene were passed through the column with the mixing ratio being gradually changed in order to obtain a gradual increase in solvency. Thus, all the copolymer fractions of lower to higher molecular weight were separated. To the eluates was added methanol to cause precipitation of the copolymers. After recovery, the polymers were dried under reduced pressure and each copolymer fraction was obtained. In the above column fractionation process, in order to prevent the possible decomposition of the copolymers, 100 ppm of Irganox® 1076 was added to the original sample and further air inside the column was replaced by nitrogen. Using each copolymer fraction, pressed sheets having about 100 to 300 μm thickness were prepared, and S.C.B. of each copolymer fraction were calculated by conducting Fourier-transform infrared absorption spectroscopy. Molecular weights of each copolymer fraction were calculated, using intrinsic viscosities [η] measured in tetralin of 135°C and the following formula

$$[\eta]=5.1\times10^{-4}.\overline{M}n^{0.725}$$

Reference Example 11

With ethylene-α-olefin copolymers of the conventional technique, a relationship between melt index (MI) and tensile impact strength was examined with melt flow ratio (MFR) used as a parameter. Results were shown in Fig 8. It is revealed that widening of molecular weight distribution results in remarkable reduction in tensile impact strength. (In the figure, molecular weight distribution was represented by MFR. Larger MFR means wider molecular weight distribution.). These ethylene-α-olefin copolymers were subjected to molecular weight fractionation with the same technique as used in Reference Example 10. All the copolymers showed trends similar to that of Reference Example 10. The fractions were divided into two groups (lower molecular weight group and higher molecular weight group) in such a way that each group became about 50% by weight, and (S.C.B. of higher molecular weight component/S.C.B. of lower molecular weight component) was calculated. It was below 0.5 in all the copolymers.

Reference Example 12

With a high pressure method polyethylene of the conventional technique and a linear, high density polyethylene of medium to low pressure method, correlations between melt index (MI) and intrinsic viscosity [η] were examined and are shown in Fig. 9. The correlation lines of each sample are clearly divided by a partition line (broken line). It is learned that the high pressure polyethylene has much lower intrinsic viscosity than that of the linear high density polyethylene of the same melt index.

A correlation between melt index and intrinsic viscosity was examined with the ethylene-α-olefin copolymers of the present invention. All of the copolymers of the present invention fell in the zone of the linear, high density polyethylene.

Claims

1. An ethylene-α-olefin copolymer composition excellent in transparency and strength and having a density of 0.915 to 0.929 g/cm^3, a melt index of 0.1 to 30 g/10 min, and a melt flow ratio of 35 to 250, which comprises 10 to 70 % by weight of at least one ethylene-α-olefin compolymer A and 90 to 30 % by weight of at least one ethylene-α-olefin copolymer B; said copolymer A having a higher molecular weight than copolymer B and being *a* copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms and having a density of 0.895 to 0.935 g/cm^3, an intrinsic viscosity $[\eta]_A$ of 1.2 to 6.0 dl/g, the number of short chain branching per 1000 carbon atoms (hereinafter abbreviated as "S.C.B.") of 7 to 40 and a (weight average molecular weight)/(number average molecular weight) value of 2 to 10; said polymer B being a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms and having a density of 0.910 to 0.955 g/cm^3, an intrinsic viscosity $[\eta]_B$ of 0.3 to 1.5 dl/g, S.C.B. of 5 to 35 and a (weight average molecular weight)/(number average molecular weight)value of 2 to 10; said copolymer A and said copolymer B being selected in order to satisfy a condition that (S.C.B. of said copolymer A)/(S.C.B. of said copolymer B) is 0.6 to 1.7 and $[\eta]_A/[\eta]_B$ is 1.75 to 6.35, which copolymer composition has a g^*_η of at least 0.9 and has a ratio of (SCB of higher molecular weight components)/(SCB of lower molecular weight components) of 0.6 to 0.8, wherein these SCB values are obtained by: obtained a curve of molecular weight distribution by gel permeation chromatography, wherein the abscissa is the logarithm of chain length (unit nm) calibrated with a standard polystyrene sample, and the ordinate is relative weight fraction; then obtaining fractions of lower and higher molecular weight by either one of the following methods :

1. in cases where curves of molecular weight distributions have one peak a lower molecular weight components side and a higher molecular weight components side are divided by a perpendicular line drawn at the peak of the curve; and the ratio of areas of these two sides is the weight ratio of lower and higher molecular weight components; separately, fractions of the same sample are prepared by column fractionation; these fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions become closest to the weight ratio obtained above;
2. in cases where curves of molecular weight distributions have two peaks including shoulders, a tangent line is drawn between the main two peaks of the higher molecular weight components side or between one peak and a shoulder of the same side, and then a perpendicular is drawn from a point where the distance between the GPC curve and the tangent line becomes largest this perpendicular splits the lower molecular weight components side and the higher molecular weight components side, and the ratio of areas of these two sides becomes the weight ratio of these two components portions; separately, fractions of the same sample are prepared by column fractionation; these fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions becomes closest to the weight ratio thus obtained; and then measuring the SCB of each group.

2. An ethylene-α-olefin copolymer composition according to Claim 1, wherein at least one of said copolymer A and said copolymer B is one member selected from the group consisting of an ethylene-butene-1 copolymer, an ethylene-4-methyl-pentene-1 copolymer, an ethylene-α-hexene-1 copolymer and an ethylene-octene-1 copolymer.

3. An ethylene-α-olefin copolymer composition according to Claim 1 or 2, wherein said copolymer composition is prepared by a multi-stage polymerization.

4. An ethylene-α-olefin copolymer composition according to Claim 1, 2 or 3, characterized in that said copolymer components are mixed as a result of a two stage polymerization wherein, in the first stage, said copolymer A is polymerized under certain polymerization conditions for a certain length of time and successively, in the second stage, said copolymer B is polymerized with the first stage polymerization conditions changed other than catalysts until an intended weight ratio of copolymers A and B is obtained.

Patentansprüche

1. Ethylen/α-Olefin-Mischpolymerisatmasse hervorragender Durchsichtigkeit und Festigkeit mit einer Dichte von 0,915 bis 0,929 g/cm^3, einem Schmelzindex von 0,1 bis 30 g/10 min. und einem Schmelzflußverhältnis von 35 bis 250, die 10 bis 70 Gewichtsprozent mindestens eines Ethylen/α-Olefin-Mischpolymers A und 90 bis 30 Gewichtsprozent mindestens eines Ethylen/α-Olefin-Mischpolymers B enthält, wobei das Mischpolymer A ein höheres Molekulargewicht aufweist als das Mischpolymer B und aus einem Mischpolymer aus Ethylen und einem α-Olefin von 3 bis 18 Kohlenstoffatomen einer Dichte von 0,895 bis 0,935 g/cm^3, einer Strukturviskosität $[\eta]_A$ von 1,2 bis 6,0 dl/g, einer Anzahl kurzkettiger Verzweigungen pro 1.000 Kohlenstoffatome (im folgenden als "S.C.B." abgekürzt) von 7 bis 40 und eines Gewichtsmittelmolekulargewicht/Zahlmittelmolekulargewicht-Werts von 2 bis 10 besteht, das Mischpolymer B aus einem Mischpolymer aus Ethylen und einem α-Olefin mit 3 bis 18 Kohlenstoffatomen einer Dichte von 0,910 bis 0,955 g/cm^3, einer Strukturviskosität $[\eta]_B$ von 0,3 bis 1,5 dl/g, einer S.C.B. von 5 bis 35 und eines Gewichtsmittelmolekulargewicht/Zahlmittelmolekulargewicht-Werts von 2 bis 10 besteht, und das Mischpolymer A und das Mischpolymer B derart ausgewählt sind, daß die Bedingung (S.C.B. des Mischpolymers A)/ (S.C.B. des Mischpolymers B) gleich 0,6 bis 1,7 und $[\eta]_A/[\eta]_B$ gleich 1,75 bis 6,35 erfüllt ist, wobei die Mischpolymerisatmasse einen g_η^*-Wert von mindestens 0,9 und ein Verhältnis (S.C.B. der Komponenten mit höherem Molekulargewicht)/(S.C.B. der Komponenten mit niedrigerem Molekulargewicht) von 0,6 bis 0,8 aufweist und wobei die S.C.B.-Werte durch Aufstellen einer Molekulargewichtsverteilungskurve, bei der auf der Abszisse der Logarithmus der Kettenlänge, geeicht mit einer Standardpolystyrolprobe, (Einheit nm) und auf der Ordinate die relative Gewichtsfraktion aufgetragen sind, mittels Geldurchdringungschromatographie und anschließendes Gewinnen von Fraktionen niedrigeren und höheren Molekulargewichts nach einer der folgenden Methoden:

1.) In Fällen, in denen Molekulargewichtsverteilungskurven einen Peak aufweisen, werden Komponenten auf der niedrigeren Molekulargewichtsseite und Komponenten auf der höheren Molekulargewichtsseite durch eine am Kurvenpeak gezogene Senkrechte geteilt. Das Verhältnis der Flächen dieser beiden Seiten ist das Gewichtsverhältnis von niedriger- und höhermolekularen Komponenten. Getrennt (davon) werden durch Säulenfraktionierung Fraktionen derselben Probe hergestellt. Diese Fraktionen werden in zwei Portionen niedriger- und höhermolekularer Komponenten vereinigt, um das Gewichtsverhältnis dieser beiden Portionen möglichst nahe an das obige Gewichtsverhältnis zu bringen;

2.) In Fällen, in denen Molekulargewichtsverteilungskurven zwei Peaks mit Schultern aufweisen, wird zwischen den beiden Hauptpeaks der Komponenten auf der höheren Molekulargewichtsseite oder zwischen einem Peak und einer Schulter auf derselben Seite eine Tangente und anschließend an einer Stelle, wo der Abstand zwischen der GPC-Kurve und der Tangente am größten wird, eine Senkrechte gezogen. Diese Senkrechte spaltet die Komponenten auf der niedrigeren Molekulargewichtsseite und die Komponenten auf der höheren Molekulargewichtsseite auf. Das Verhältnis der Flächen dieser beiden Seiten ist das Gewichtsverhältnis von niedriger- und höhermolekularen Komponenten. Getrennt (davon) werden durch Säulenfraktionierung Fraktionen derselben Probe hergestellt. Diese Fraktionen werden in zwei Portionen niedriger- und höhermolekularer Komponenten vereinigt, um das Gewichtsverhältnis dieser beiden Portionen möglichst nahe an das obige Gewichtsverhältnis zu bringen.

2. Ethylen/α-Olefin-Mischpolymerisatmasse nach Anspruch 1, dadurch gekennzeichnet, daß mindestens eines der Mischpolymere A und B aus einem Ethylen/Buten-l-Mischpolymer, Ethylen-4-Methylpenten-1-Mischpolymer, Ethylen-α-Hexen-1-Mischpolymer oder Ethylen/Octen-1-Mischpolymer besteht.

3. Ethylen/α-Olefin-Mischpolymerisatmasse nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß sie durch mehrstufige Polymerisation hergestellt ist.

4. Ethylen/α-Olefin-Mischpolymerisatmasse nach Ansprüchen 1, 2 oder 3, dadurch gekennzeichnet, daß die Mischpolymerisatkomponenten als Ergebnis einer zweistufigen Polymerisation gemischt werden, wobei in der ersten Stufe das Mischpolymer A unter bestimmten Polymerisationsbedingungen eine bestimmte Zeit lang polymerisiert wird und anschließend in der zweiten Stufe das Mischpolymer B unter Änderung der Polymerisationsbedingungen der ersten Stufe mit Ausnahme der Katalysatoren polymerisiert wird, bis ein gewünschtes Gewichtsverhältnis der Mischpolymere A und B erreicht ist.

Revendications

1. Composition à base de copolymères éthylène/α-oléfines présentant d'excellentes propriétés de transparence et de résistance mécanique et ayant une masse volumique de 0,915 à 0,929 g/cm^3, un indice de fusion de 0,1 à 30 g/10 mn et un rapport d'écoulement à l'état fondu de 35 à 250, comprenant 10 à 70 % en poids d'au moins un copolymère A éthylène/α-oéfine et 90 à 30 % en poids d'au moins un copolymère B éthylène/α-oléfine, le copolymère A ayant un poids moléculaire plus élevé que le copolymère B et étant un copolymère d'éthylène et d'une α-oléfine à 3-18 atomes de carbone, ayant une masse volumique de 0,895 à 0,935 g/cm^3, une viscosité intrinsèque [η] A de 1,2 à 6,0 dl/g, un nombre de branches à courte chaîne pour 1000 atomes de carbone (ci-après désigné par l'abréviation « S.C.B. ») de 7 à 40 et une valeur (poids moléculaire moyen en poids/poids moléculaire moyen en nombre) de 2 à 10, le copolymère B étant un copolymère d'éthylène et d'une α-oléfine à 3-18 atomes de carbone, ayant une masse volumique de 0,910 à 0,955 g/cm^3, une viscosité intrinsèque $[\eta]_B$ de 0,3 à 1,5 dl/g, un S.C.B. de 5 à 35 et une valeur (poids moléculaire moyen en poids/poids moléculaire moyen en nombre) de 2 à 10, le copolymère A et le copolymère B étant choisis de manière à satisfaire la condition que (S.C.B. du copolymère A)/(S.C.B.) du copolymère B est 0,6 à 1,7 et $[\eta]_A/[\eta]_B$ est 1,75 à 6,35, laquelle composition à base de copolymères a un $g\eta^*$ d'au moins 0,9 et un rapport (S.C.B. des composants de haut poids moléculaire/S.C.B. des composants de bas poids moléculaire) de 0,6 à 0,8, ces valeurs S.C.B. étant obtenues : en obtenant une courbe de distribution des poids moléculaires par chromatographie de perméation de gel, l'abscisse étant le logarithme de la longueur de chaîne (unité : nm) calibrée avec un échantillon de polystyrène étalon et l'ordonnée étant la fraction pondérale relative ; puis en obtenant les fractions de bas et haut poids moléculaires par l'une ou l'autre des méthodes suivantes :

1/ dans les cas où les courbes de distribution des poids moléculaires présentent un seul pic, le côté des composants de poids moléculaires plus bas et le côté des composants de poids moléculaires plus élevés sont séparés par une ligne perpendiculaire au pic de la courbe ; et le rapport des aires de ces deux côtés est le rapport en poids des composants de poids moléculaires plus bas et plus élevés ; séparément, des fractions du même échantillon sont préparées par fractionnement en colonne ; ces fractions sont rassemblées en deux parties de composants de poids moléculaires plus bas et plus élevés, de telle manière que le rapport en poids de ces deux parties soit très proche du rapport en poids obtenu ci-dessus ;
2/ dans les cas où les courbes de distribution des poids moléculaires présentent deux pics comportant des

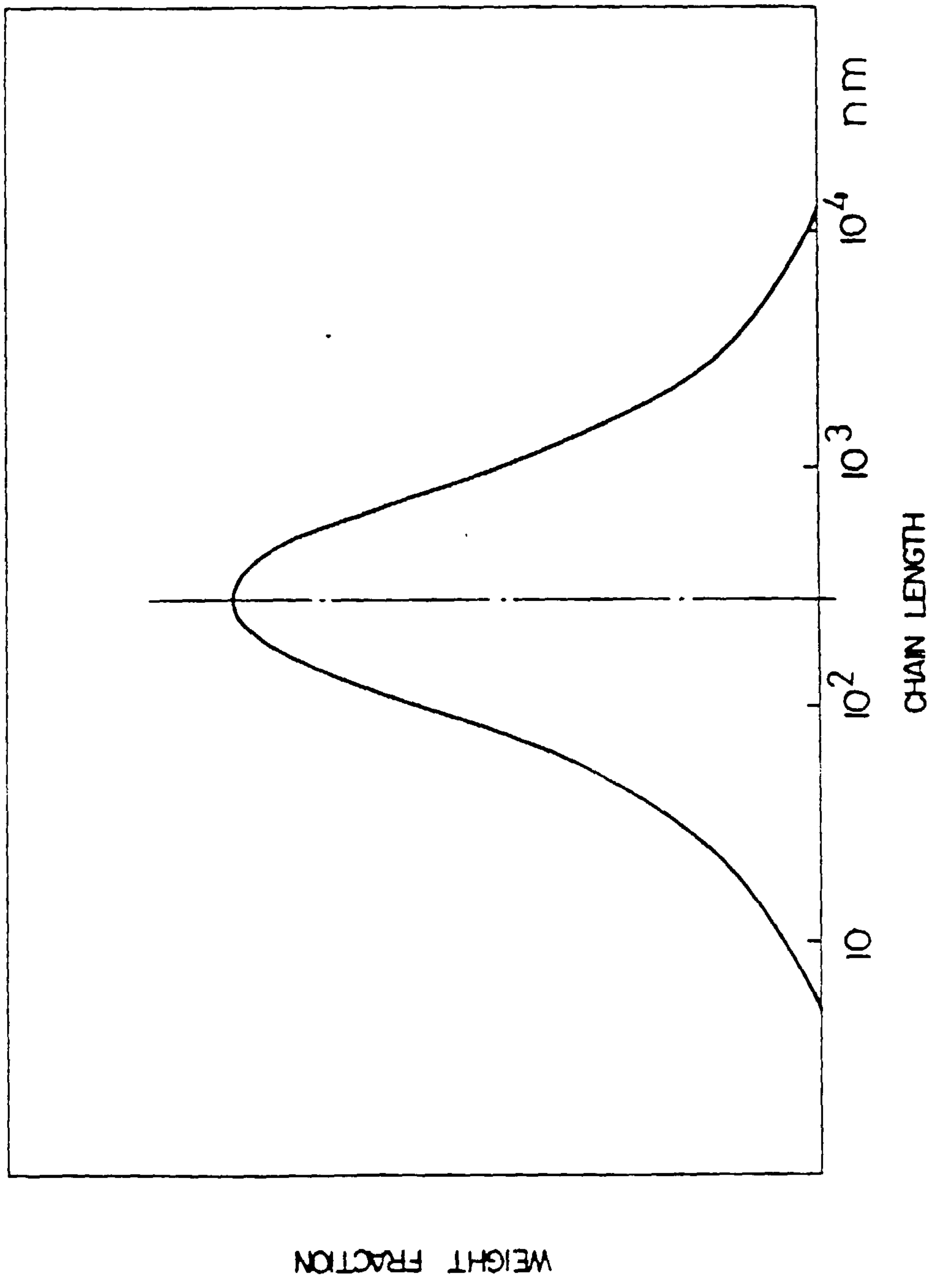
épaulements, une ligne tangente est tracée entre les deux pics principaux du côté des composants de poids moléculaires plus élevés ou entre un pic et un épaulement du même côté, puis une perpendiculaire est tracée à partir du point où la distance entre la courbe de CPG et la tangente atteint un maximum ; cette perpendiculaire sépare le côté des composants de plus bas poids moléculaires et le côté des composants de poids moléculaires plus élevés et le rapport des aires de ces deux côtés devient le rapport en poids de ces deux parties de composants ; séparément, des fractions du même échantillon sont préparées par fractionnement en colonne ; ces fractions sont rassemblées en deux parties de composants de poids moléculaires plus bas et plus élevés, de telle manière que le rapport en poids de ces deux parties soit très voisin du rapport en poids ainsi obtenu ;
puis en mesurant la S.C.B. de chaque groupe.

2. Composition à base de copolymères éthylène/α-oléfines selon la revendication 1, dans laquelle l'un au moins du copolymère A et du copolymère B est choisi parmi les membres du groupe constitué par un copolymère éthylène/butène-1, un copolymère éthylène/4-méthylpentène-1, un copolymère éthylène/hexène-1 et un copolymère éthylène/octène-1.

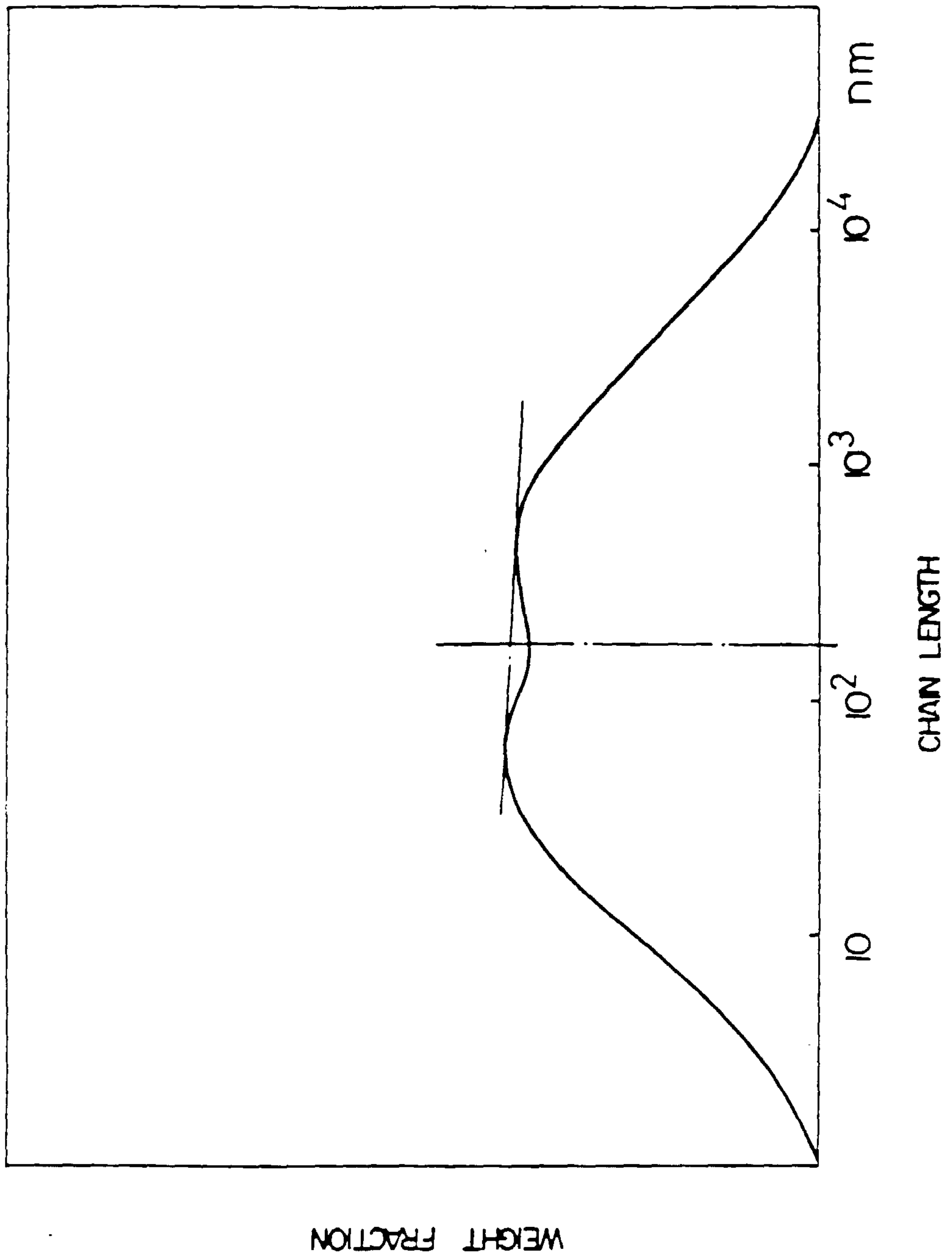
3. Composition à base de copolymères éthylène/α-oléfines selon la revendication 1 ou 2, caractérisée en ce qu'elle est préparée par une polymérisation à plusieurs stades.

4. Composition à base de copolymères éthylène/α-oléfines selon l'une quelconque des revendications 1 à 3, caractérisée en ce que les composants du copolymère sont mélangés en conséquence d'une polymérisation à deux stades dans laquelle, dans le premier stade, le copolymère A est polymérisé dans certaines conditions de polymérisation pendant une certaine période de temps, puis, dans le second stade, le copolymère B est polymérisé dans des conditions qui, en dehors des catalyseurs, sont modifiées par rapport à celles du premier stade, jusqu'à ce qu'un rapport de poids voulu des copolymères A et B soit obtenu.

FIG. 1



F I G. 2



F I G. 3

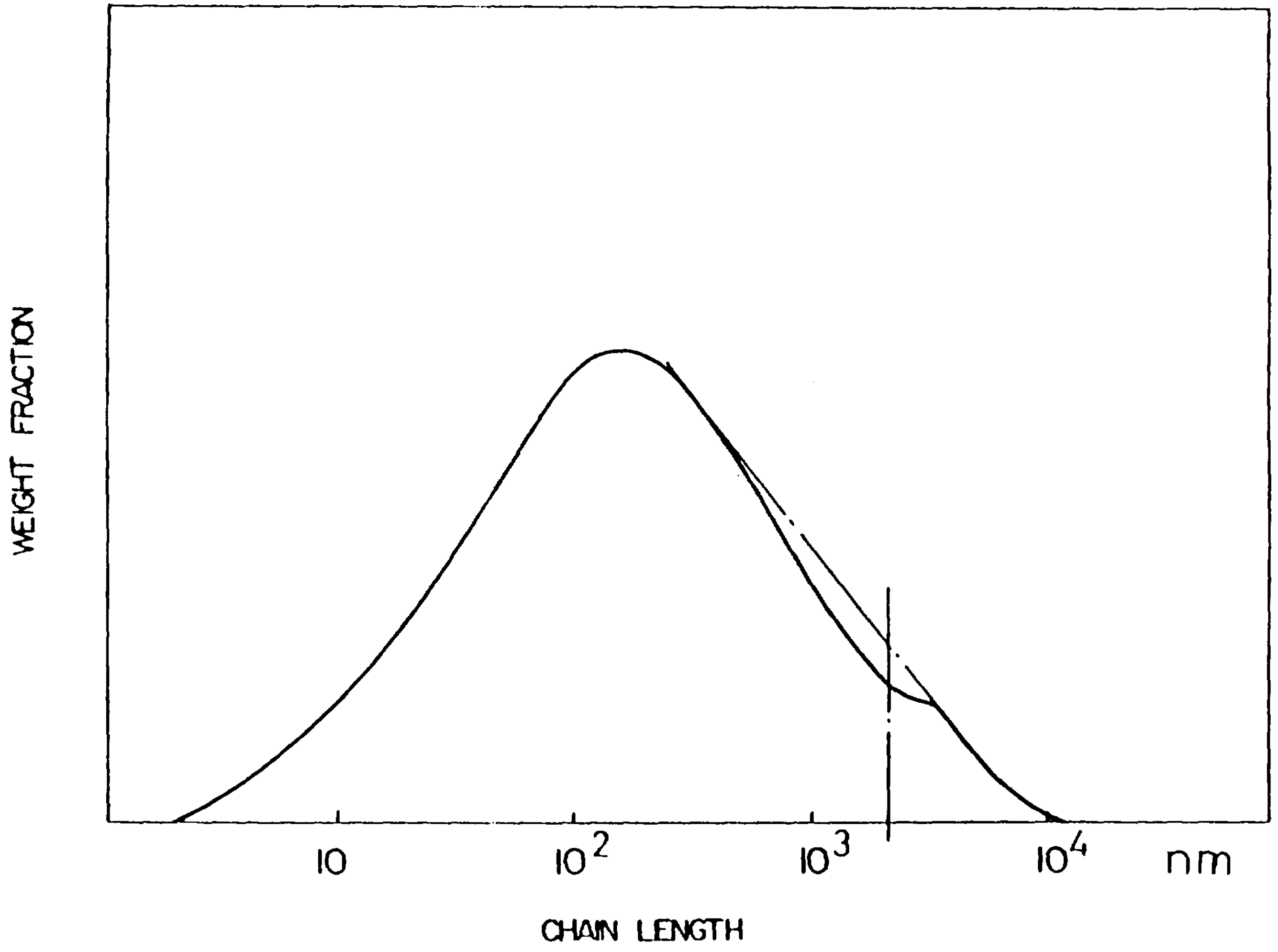
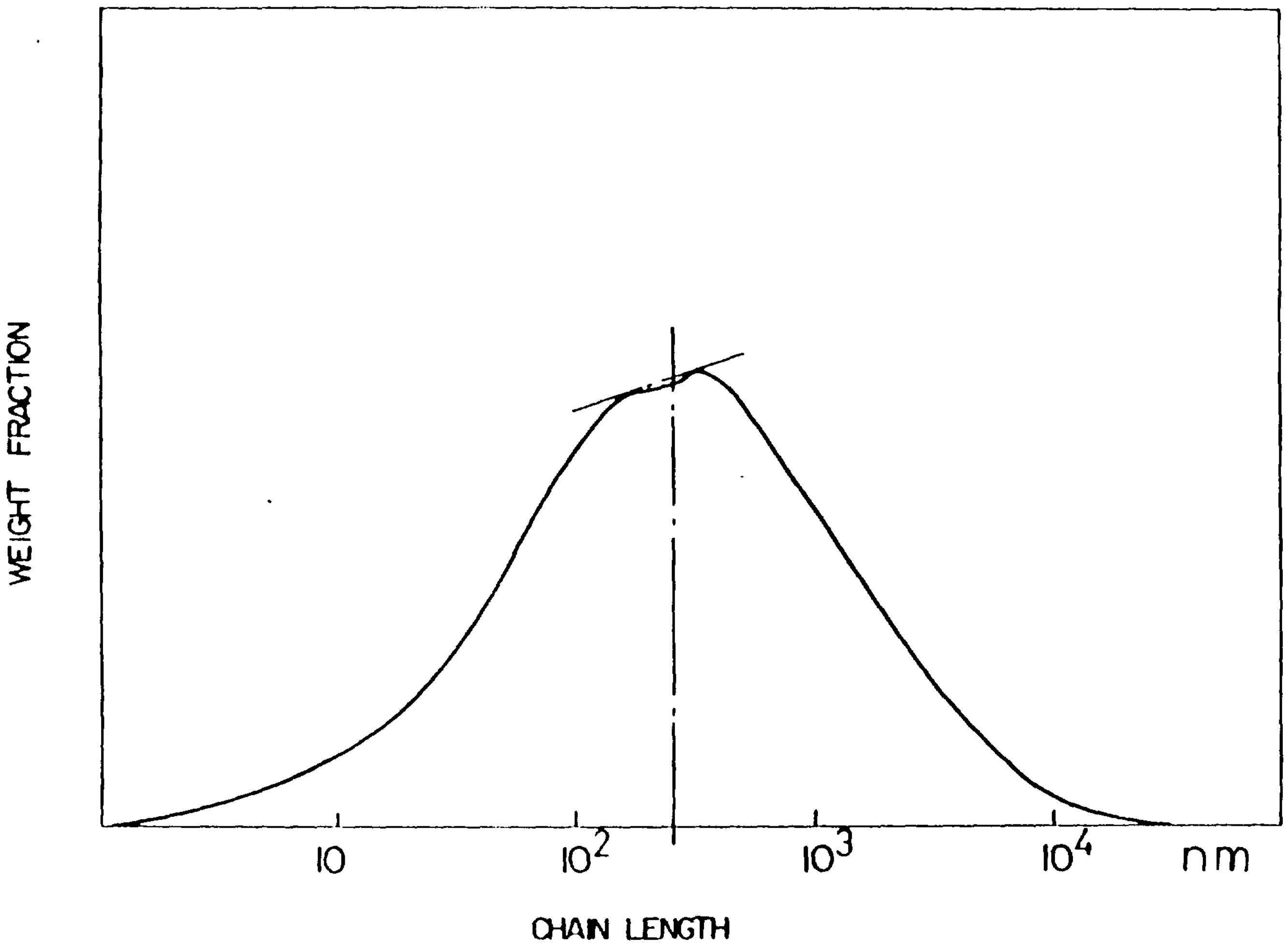


FIG. 4



F I G. 5

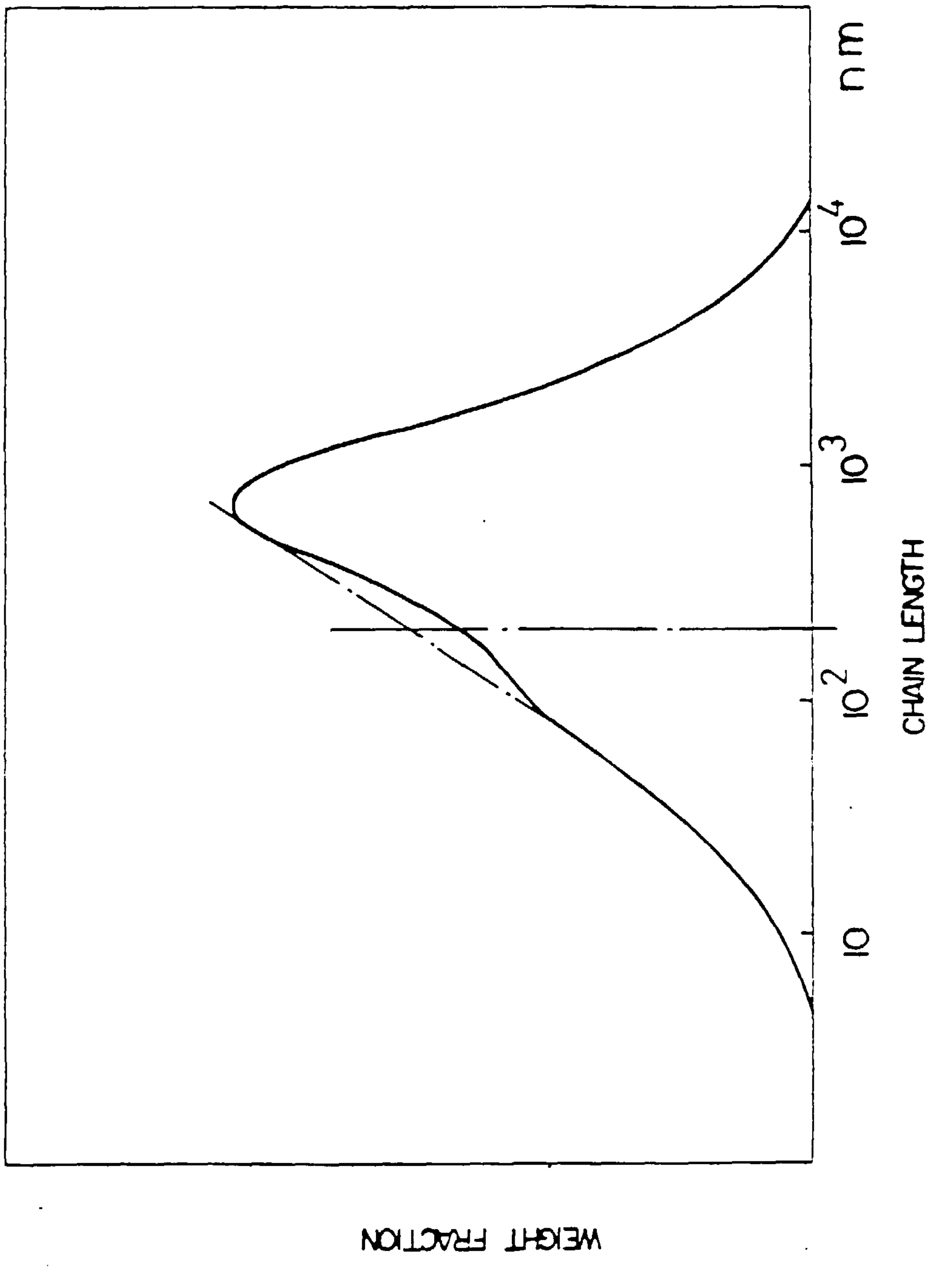


FIG. 6

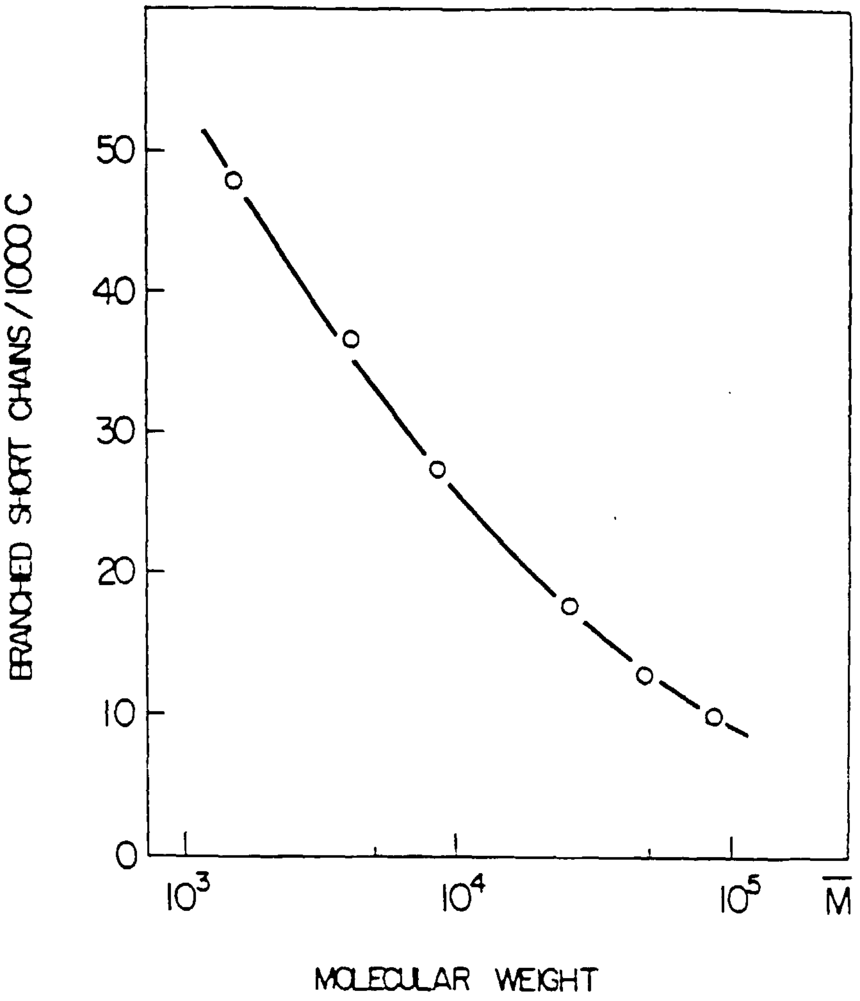

BRANCHED SHORT CHAINS / 1000 C
50
40
30
20
10
0
10^3
10^4
10^5
M̄
MOLECULAR WEIGHT

FIG. 7

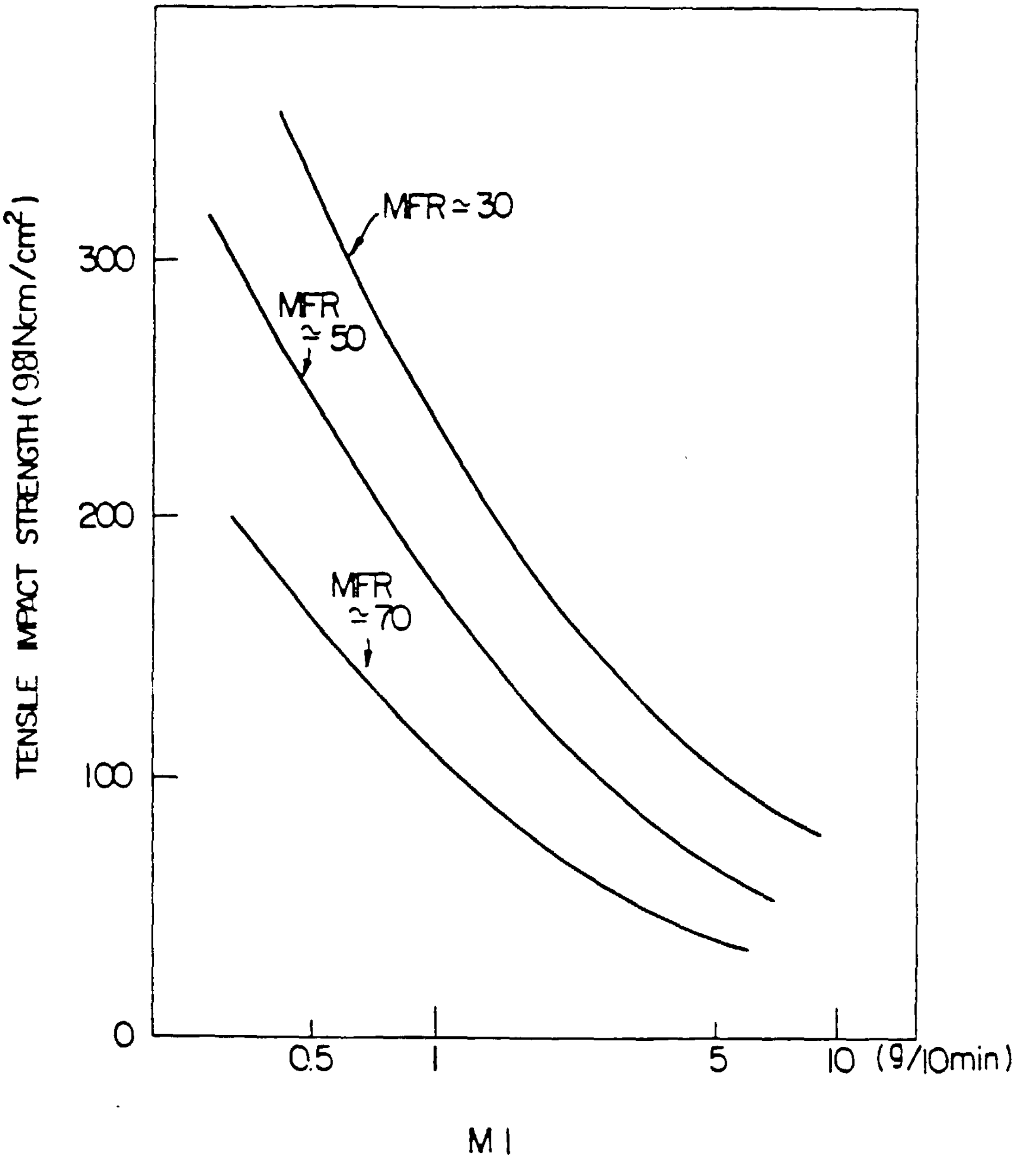
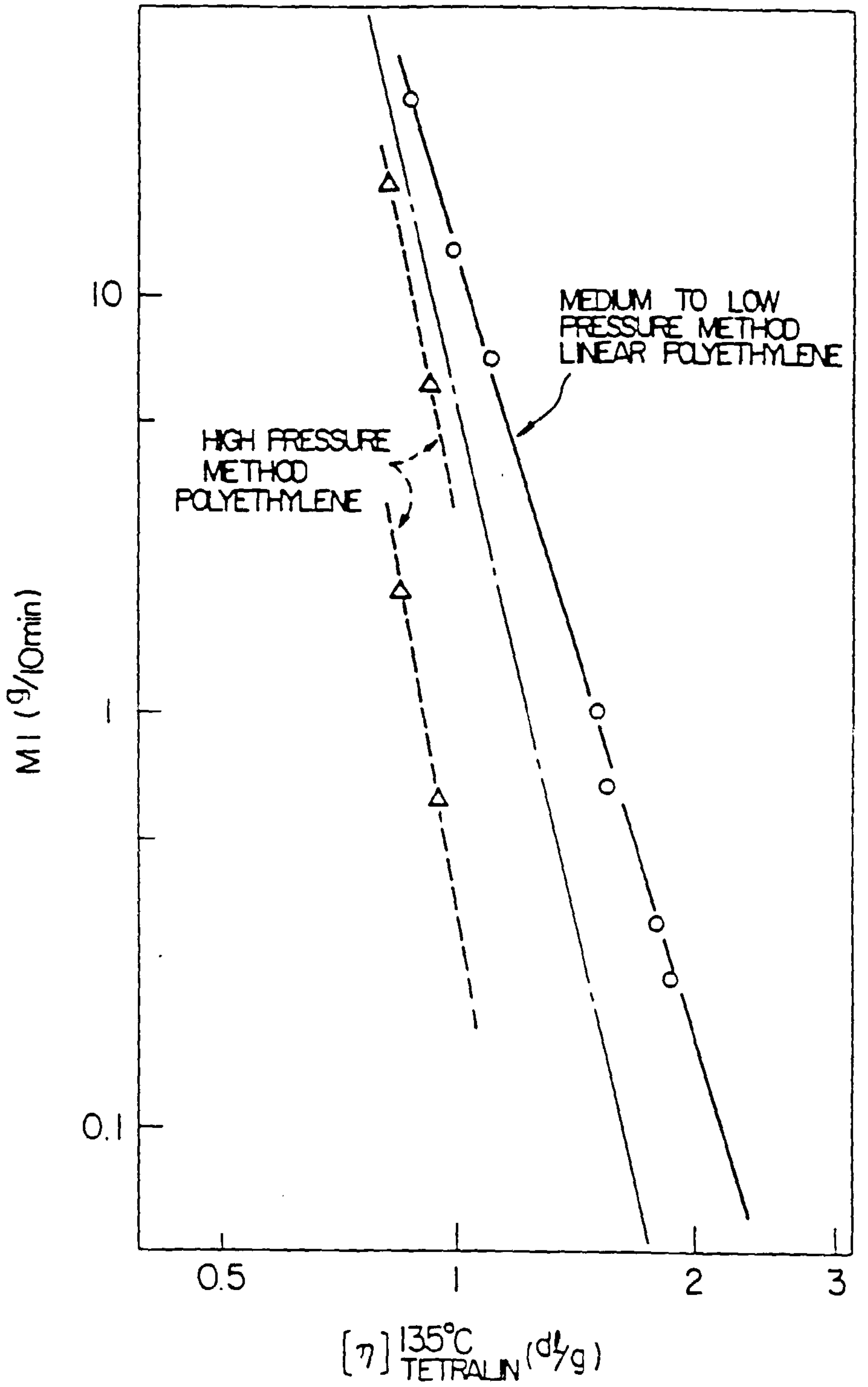

TENSILE IMPACT STRENGTH (9.81Ncm/cm^2)
300
200
100
0
0.5
1
5
10 (g/10min)
MI
MFR ≃ 30
MFR ≃ 50
MFR ≃ 70

FIG. 8


10
1
0.1
MI (g/10min)
0.5
1
2
3
[η] 135°C TETRALIN (dl/g)
MEDIUM TO LOW PRESSURE METHOD LINEAR POLYETHYLENE
HIGH PRESSURE METHOD POLYETHYLENE